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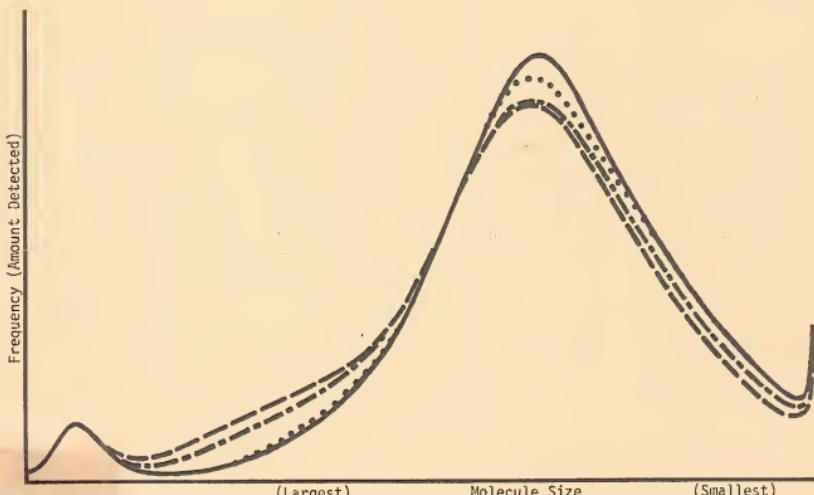
USE OF HIGH PRESSURE LIQUID CHROMATOGRAPHY
TO DETERMINE THE EFFECTS OF VARIOUS ADDITIVES AND FILLERS
ON THE CHARACTERISTICS OF ASPHALT

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Prepared for
MONTANA DEPARTMENT OF HIGHWAYS
RESEARCH PROGRAM

In cooperation with
U.S. DEPARTMENT OF TRANSPORTATION
FEDERAL HIGHWAY ADMINISTRATION



MOLECULE SIZE/FREQUENCY DISTRIBUTIONS FOR ASPHALT SAMPLES AS DETERMINED BY HPLC

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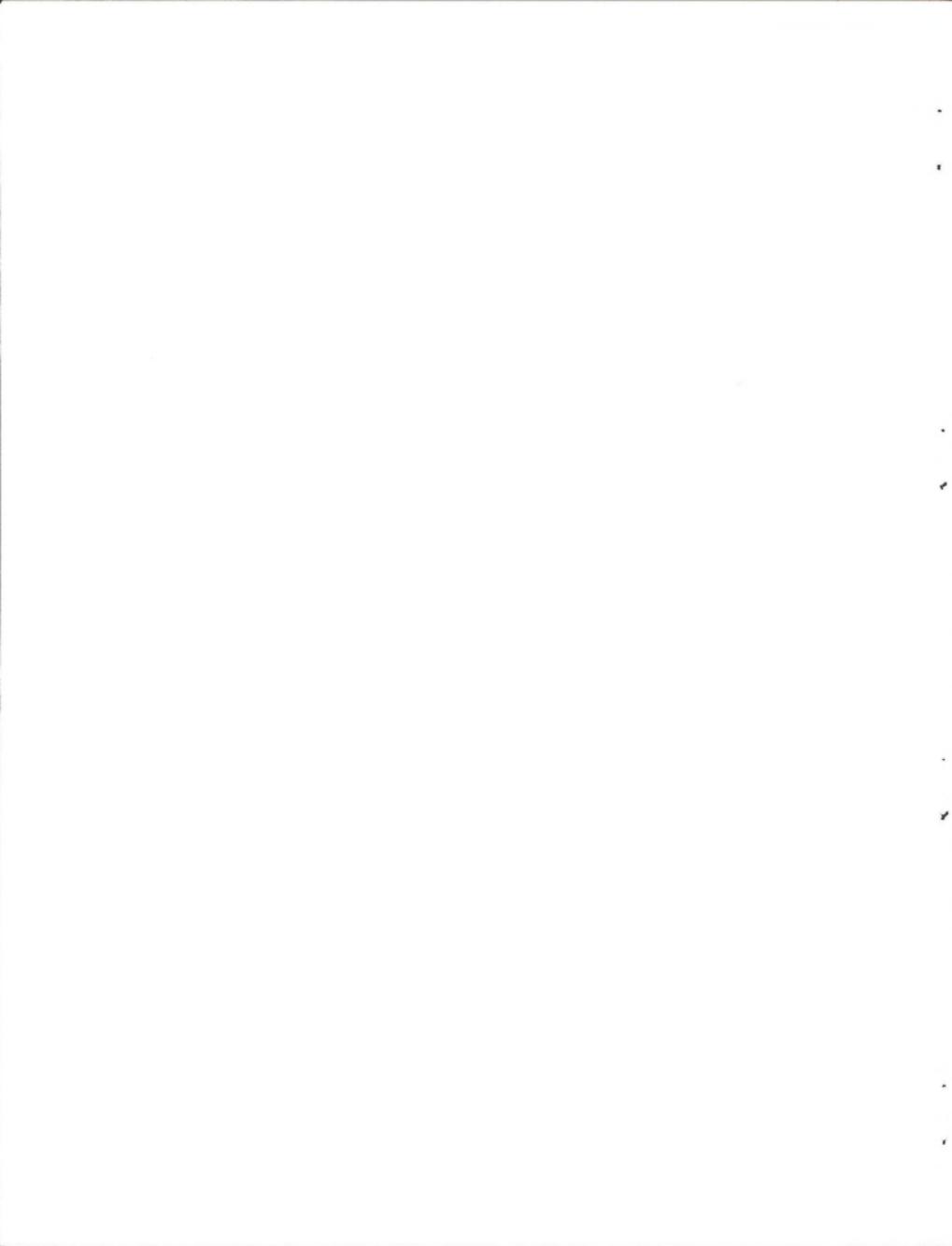
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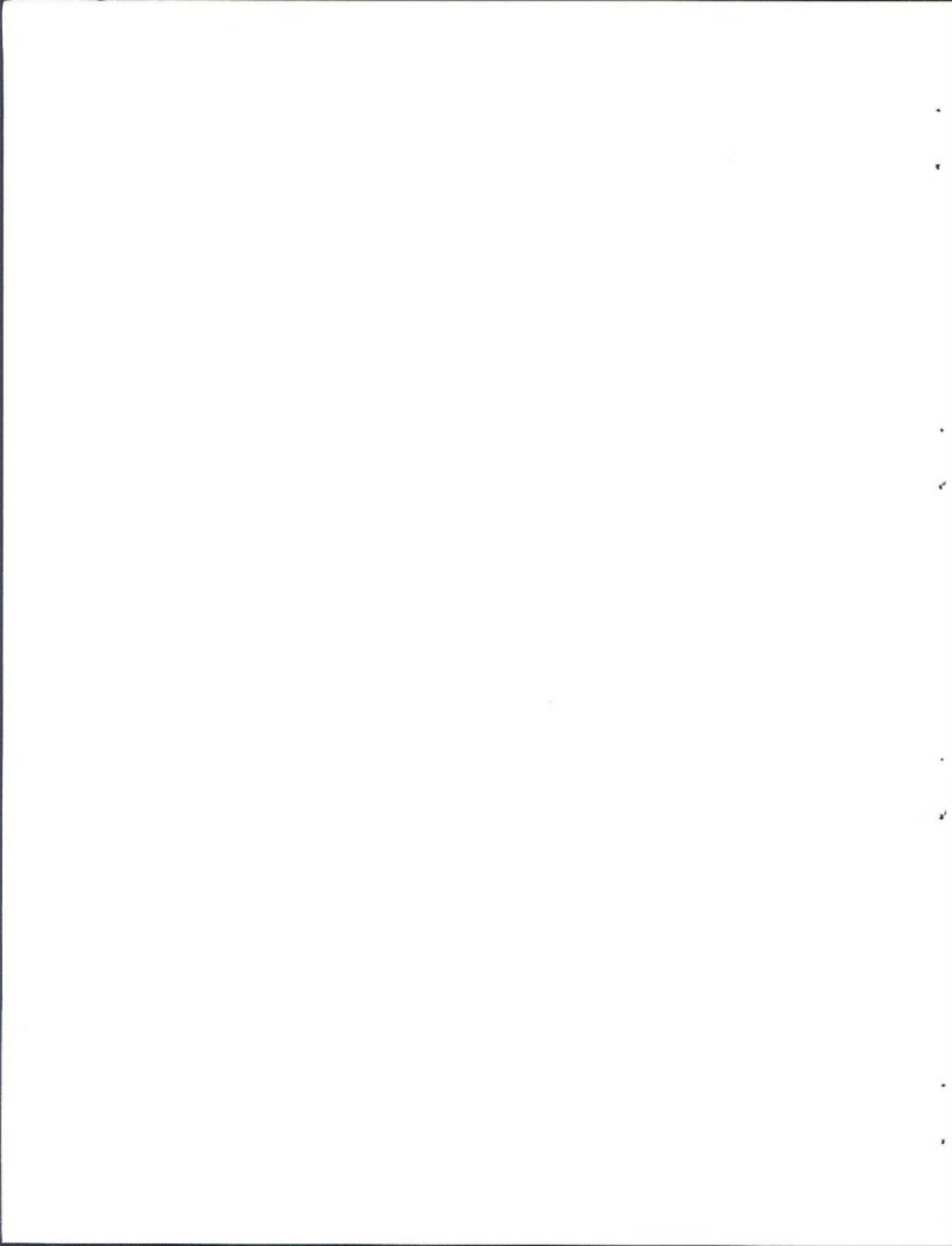
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Contents

Disclaimer Statement	i
Abstract	ii
Introduction	1
Background	1
Summary of previous projects	2
Objectives	4
Review of data interpretation	5
Results and Discussion	9
I. Refinement of methods	9
A. Extraction methods - ultrasonification	9
B. Extraction methods - comparison with MDOH method	9
C. Column selection	11
D. Effects of solvents used for mobile phase	12
E. Use of uv detector	18
1) Comparison of uv with RI detection	18
2) Isolation of LMS, MMS and SMS fractions	22
3) Summary of Section E	23
F. Precision	24
II. Use of the model asphalt	25
III. Laboratory simulation of field effects	27
IV. Effects of heating, additives and fillers	35
A. Heat	35
B. Aggregates	36
C. Hydrated lime	41
D. Fly ash	43
E. Antistripping agents	47
F. Sulfur	51
G. Rubber	53
H. Carbon black	54
J. Summary of Section IV	56
V. Aging of asphalts in pavements	59
VI. Performance prediction/shadow specification	62
VII. Recycling	75
VIII. Test sections	87
IX. Conclusions	88

Appendix

A.	Extraction method	91
B.	Methods for laboratory simulation of field effects	92
C.	Methods for determination of heating and additive effects	93
D.	Methods for analysis by HP-GPC	95
E.	Petrographic analyses of sample aggregates	96
References		97

DISCLAIMER STATEMENT

The contents of this report reflect the views of the authors who are responsible for the facts and the accuracy of the data presented herein. The contents do not necessarily reflect the official views or policies of the Montana Department of Highways or the Federal Highway Administration. This report does not constitute a standard specification or regulation.



ABSTRACT

This project, third in a series, dealt with the molecular composition of asphalts (i.e., molecular size/frequency distributions), and with the changes in asphalt composition that have been found to result from the inclusion of aggregate, additives, fillers and extenders in bituminous paving mixtures under normal production conditions in Montana. These molecular size distributions for asphalt are determined by High Pressure Liquid Chromatography in the Gel Permeation Mode, a method adapted and improved earlier in this work. This method has interchangeably been described as either "HPLC" or "HP-GPC", though the latter is now preferred. There has been no substantive change in the instrumentation or method of analysis employed in this series of projects, however.

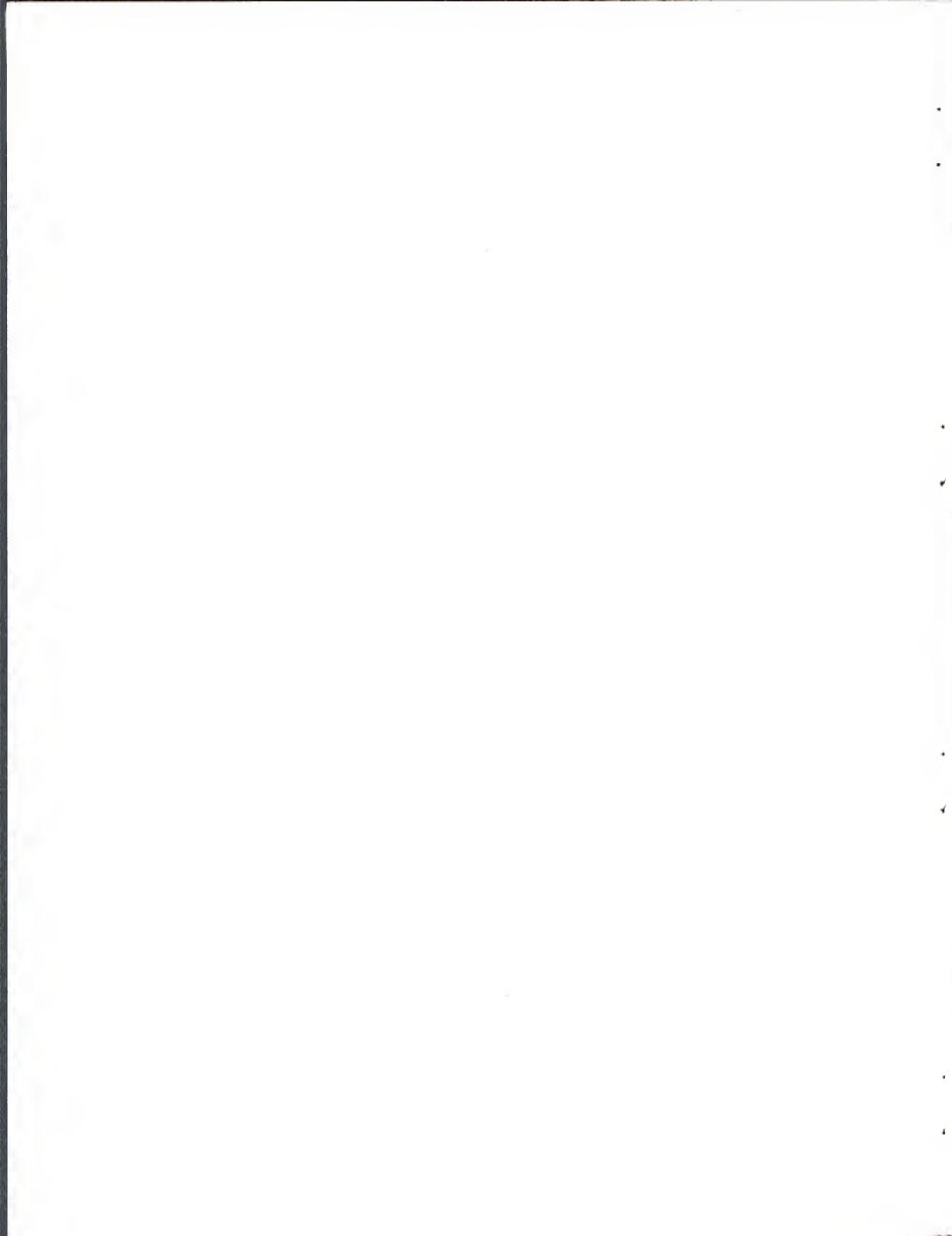
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NOTE

The casual reader who may not wish to pursue the details involved in this report is directed to the conclusions given in Section IX, page 87.



INTRODUCTION

BACKGROUND

The causes of cracking or of other forms of asphaltic pavement distress are many and varied: subgrade failure, aggregate quality and climatic conditions are examples. During recent years, the asphalt cement itself has come under closer scrutiny as a possible villain in the case.

Are there characteristics of asphalt cement that can be linked to pavement quality? Are all asphalt cements that share a penetration grade and/or a viscosity rating truly alike? Do aggregates, additives and fillers change the asphalt and thereby affect its performance? Do the crude oil and refinery processes affect the quality of the asphalt? These and other such questions have led several people to study asphalt cement by various methods. The same questions prompted us to undertake a project under the sponsorship of the Montana Department of Highways (MDOH). Since 1976, we have been using High Pressure Liquid Chromatography in the gel permeation mode (HP-GPC) to study Montana asphalts. Because cracking is one of the major problems affecting the longevity of asphaltic pavements in the state of Montana, the studies have concentrated on the relationship between HP-GPC data and cracking of pavement. Results of two earlier projects will be summarized in the next section. The remainder of this report will be devoted to discussion of the most recent work done for MDOH.

SUMMARY OF PREVIOUS PROJECTS

In HPLC using gel permeation columns (HP-GPC), molecules in a mixture are separated according to size. During the first project, (1) a number of asphalts obtained from established roadways which ranged in quality from good to bad with regard to cracking, were analyzed by this method. The resulting data showed that asphalts differed significantly in molecular size distribution. Furthermore, these differences appeared to be related to performance. These early results seemed promising enough to warrant further study.

A second project (2) was undertaken to refine the method and to broaden the investigation of the correlation between molecular size distribution and performance of asphalts in established roadways. During the course of the project, improvements were made in methods of sample preparation, sample analysis and data analysis.

That investigation showed that the molecular size distributions of asphalts from the best Montana roadways are virtually identical. Furthermore, the chromatograms of asphalts from inferior roadways showed differences from those of excellent roadways which are roughly proportional to the degree of cracking failure of the pavement. This information permitted the selection of an asphalt model which was representative of Montana's best roadways. Asphalts which closely match the molecular size distribution of this model should perform well under conditions found in Montana.

The potential utility of the HP-GPC method was demonstrated in other ways during the project. It was used to characterize the asphalts produced by each of Montana's refineries. The method indicated that changes are induced in an asphalt by the addition of aggregate, lime or other

materials as well as by the processes used in road building. The method also appeared to have promise in the design of recycling projects. HP-GPC was shown to be a more accurate measure of asphalt quality than asphaltenes content, penetration or ductility.

Finally during the second project, an ongoing study was established to follow the effects of aging on a number of new roads.

Although the second project demonstrated the correlation of molecular size distribution with asphalt performance for Montana, it raised a number of crucial questions. For example, it was shown that the process of preparing a plant mix causes changes in the molecular size profile of an asphalt. However, the limited sampling could not show whether or not such changes would be consistent from asphalt to asphalt or aggregate to aggregate. A similar uncertainty existed for the effect of addition of lime to a plant mix.

In other words, the model for finished asphalt, (that is, asphalt extracted from a completed pavement) was well established, but the model for the untreated asphalt would depend upon consideration of the accumulation of the effects of processing and additives. On the other hand, the fact that such changes do occur would suggest that it might be possible to engineer the asphalt to match the model profile.

The potential utility of the method in monitoring recycling projects and the aging of pavements, determining the effects of various processes and additives, as well as the further possibility that this information could then be used to improve the performance of asphalt roadways, prompted the current project.

OBJECTIVES

In order to explore the potential utility of the HP-GPC method, a number of specific goals for the current project were established. They are marked with a * below. In addition to these formal objectives, a number of other brief but important studies have also been carried out. All of these objectives in the list below will form the outline of the discussion section to follow.

- I. Continue to refine the HP-GPC method
- II. Further clarify the model
- III. Reproduce in the laboratory the effects on asphalt of processing in the field
- *IV. Determine the quantitative effects on the molecular size distribution of asphalt brought about by the following:
 - A) heat
 - B) specific aggregates
 - C) hydrated lime
 - D) fly ash
 - E) antistripping agents
 - F) sulfur
 - G) rubber
 - H) other agents as deemed necessary.
- *V. Monitor the HP-GPC profiles of the asphalts from Big Sky and other roadways studied during previous projects to determine the effects of aging on molecular size distribution.
- *VI. Using the model asphalt defined in Project II, monitor the performances of Big Sky and other roadways relative to predicted performance. Also, conduct a series of shadow specification tests on overlay paving projects.
- *VII. Determine the characteristics of asphalts in recycling projects.
- *VIII. Using data garnered from the above objectives in addition to results from the previous investigations, conduct demonstration projects during the 1981 paving season.
- IX. Conduct a search of the literature for information pertinent to our work.

REVIEW OF DATA INTERPRETATION

The HPLC system used in this study is best described as high performance gel permeation chromatography, HP-GPC. It permits the largest molecules to pass most quickly through the columns but successively retards the progress of smaller molecules. This is reflected in the sample chromatograms, Figure 1. The elution time is recorded in minutes along the ordinate. The largest molecules elute within the shortest time and, therefore, appear on the left.

The small peak at the far left, A, represents a standard monodisperse polystyrene. The spike on the right, G, results from toluene. Both of these materials are added to each sample to serve as internal standards. Their purpose is two fold: first, to aid in monitoring the performance of the HP-GPC system; second, to aid in the visual comparison of chromatograms. The latter is accomplished by superimposing the standard peaks as has been done in this example (Figure 1).

Region F is a variable characteristic of the system and is not part of the asphalt.

The broad peak, B-E, represents the molecular size distribution (MSD) of the asphalt. The asphalt peak elutes within 9 minutes under the conditions used. The chromatogram has been divided into 3 sections, each 3 minutes wide. Region B-C has been called the large molecular size (LMS) region; C-D represents medium molecular size (MMS); D-E is the small molecular size (SMS) region.

The data recording system used permits the calculation of the area under the peak in each of these three regions thus also permitting the calculation of the percent LMS in a given asphalt, for example.

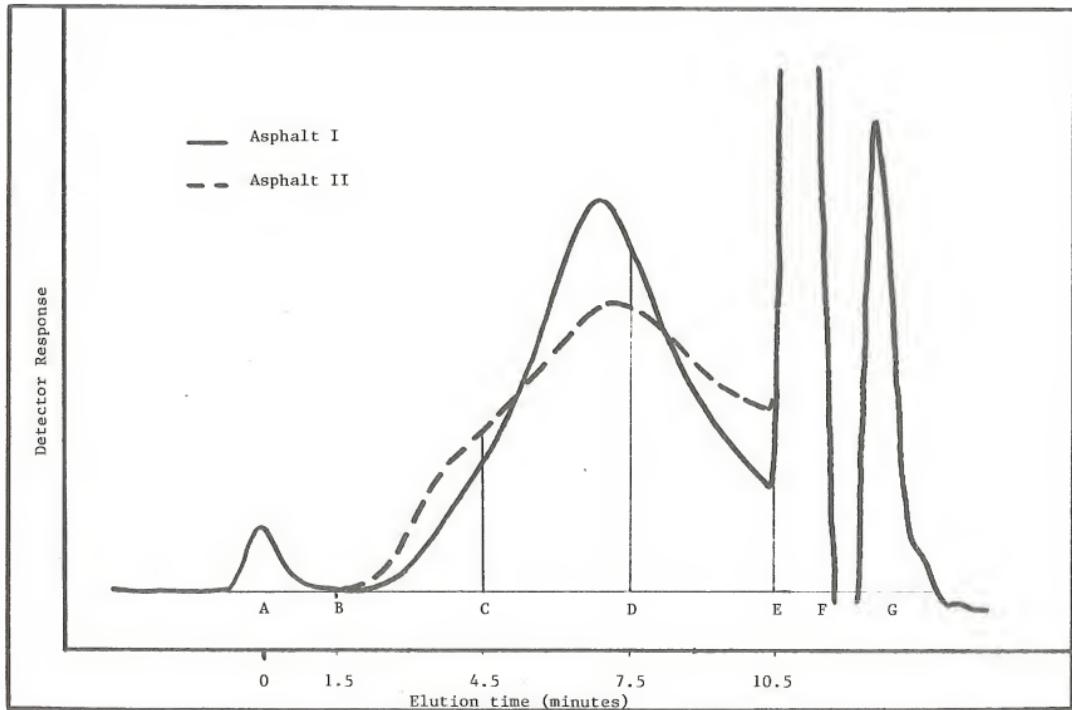


Figure 1. Interpretation of HP-GPC Chromatograms

Therefore the chromatograms may be compared mathematically as well as visually.

As exemplified in Figure 1, chromatograms may differ in one or more of the following features which may be measured both visually and mathematically:

1) Elution time of the largest molecules.

Of the two asphalts, II (dashed line) contains the largest molecules because they begin to elute earlier than large molecules of I.

2) Height of the curve in the LMS region

Asphalt II contains more LMS material at a given elution time than does Asphalt I as evidenced by the greater height of the curve for II at that point.

3) Area of the LMS region

The area percentage of the LMS region relative to the whole asphalt, is greater for asphalt II than for I. Asphalt II contains 11.4% LMS; asphalt I contains 7.7%.

4) Height of curve maximum relative to height in LMS and SMS regions.

Asphalt II contains a much higher proportion of LMS and SMS materials to MMS components than does asphalt I. This visual comparison is verified by area percentages:

$$\text{I} - 7.7\% \text{ LMS}, \quad 54.8\% \text{ MMS}, \quad 37.3\% \text{ SMS} \quad - \quad \frac{\text{LMS} + \text{SMS}}{\text{MMS}} = 0.82$$

$$\text{II} - 11.4\% \text{ LMS}, \quad 44.0\% \text{ MMS}, \quad 44.6\% \text{ SMS} \quad - \quad \frac{\text{LMS} + \text{SMS}}{\text{MMS}} = 1.27$$

5) Height of the curve in the SMS region

Asphalt I contains fewer SMS components than asphalt II. This is likewise verified by the area percentages shown in item 4 above.

These features are listed above not only in order of their appearance on the chromatogram, but also in order of their importance to asphalt quality. Work in the previous project showed that the greater the disparities between the HP-GPC chromatogram of a given asphalt and that of a standard asphalt of excellent quality, the poorer the performance of that asphalt with respect to cracking. This is especially true in the case of the size and amount of LMS material. It should be pointed out that asphalt I is from a roadway which has shown no cracking (or other forms of distress) in more than 20 years. Asphalt II is from a severely and extensively cracked pavement which was sampled at the age of 14 years.

RESULTS AND DISCUSSION

I. REFINEMENT OF METHODS

A. Extraction Methods - ultrasonification

During earlier work, a reflux method of extracting asphalt from cores was developed. Because this method is quite time-consuming, an alternative method was sought. Use of ultrasonification equipment was found to yield much more rapid and equally satisfactory removal of asphalt from aggregate (see Appendix A). It is well suited to the extraction of the small amounts of asphalt required for this study. Furthermore, HP-GPC chromatograms of asphalt extracted from a single core by either method were alike. One minor problem is that ultrasonification tends to degrade some aggregates. Therefore, careful filtration of dissolved asphalt is required in order to avoid plugging HP-GPC equipment and to obtain accurate weight of the sample to be injected.

B. Extraction methods - comparison with MDOH

Use of various solvents for the extraction process was tested in earlier projects. Benzene and THF were found to give comparable results. However, a direct comparison between the method used at MDOH laboratories [a reflux extraction using trichloroethylene, TCE(AASHTO T164-76)] and the method used for this project (ultrasonification in THF) had not been made. During this project, 2 cores from different pavements were halved vertically. Half of each core was extracted by the AASHTO method in the MDOH laboratory; the remaining half was extracted by ultrasonification in this laboratory. The results are shown in Figure 2. The extracts from pavement A (85-100/Refiner B) yielded nearly identical chromatograms whereas those from pavement B (120-150/Refiner D) showed significant differences in the LMS and MMS regions. Without delving into the

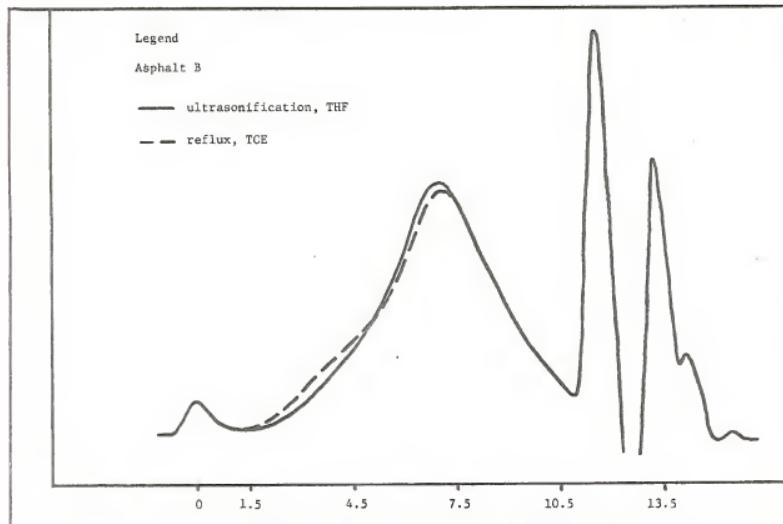
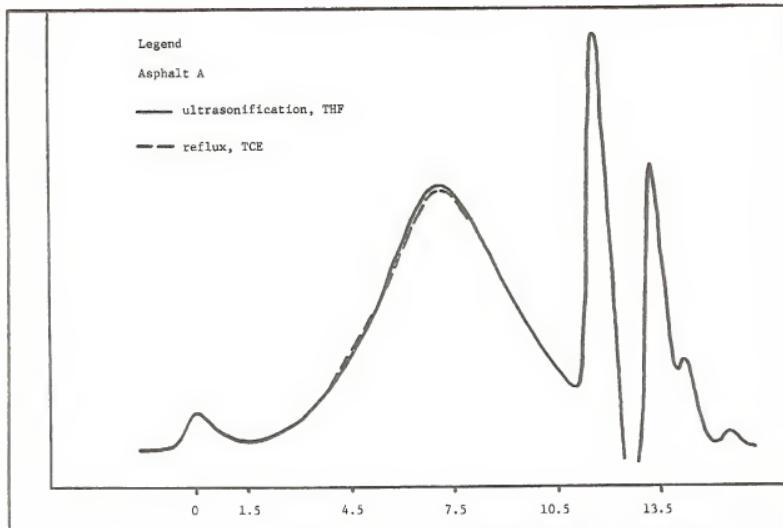


Figure 2. Comparison of Effects of Extraction Method on MSD

chemical reasons for this deviation, it suffices to say that asphalts compared by the HP-GPC method must be prepared by carefully standardized techniques. Certainly, comparison of asphalts extracted by different solvents may yield erroneous results.

C. Column selection and maintenance

μ -Styragel columns, which are used in this research, are specified by column dimensions and diameter of packing beads, both of which are constant in a given brand. Another specification is the size of pores in the beads (eg., 10^3 Å or 500 Å) which determines the maximum size of the molecules which will be retained by the column. Columns are therefore, designated by pore size.

The efficiency of an individual column is given by an experimentally-determined number called the theoretical plate count. This value varies from column to column within a group of columns of the same pore size.

Chromatographic shape is very column dependent. For example, in this work, a 10^5 Å column is responsible for separating the standard peak from the asphalt peak (see Figure 1, page 6). A 10^3 Å column defines the LMS region while 4 -500 Å units delineate smaller molecules. Chromatographic shape is, apparently, also dependent upon the theoretical plate counts of the individual columns, but experience does not yet permit quantifying the effect.

The manufacturer of these columns (Waters, Assoc.) does not presently control quality so that all columns of a given size have the same number of theoretical plates. However, they will supply columns within a specified range of plate counts upon request. Nevertheless, it is also true that plate counts change slowly as columns are used. To

overcome these problems, several steps must be taken.

- 1) Manufacturer's instructions regarding handling and care of columns, eg., pressure limits, solvent compatibility, etc., must be rigorously followed.
- 2) Samples must be filtered through a 10μ filter (or smaller) to remove particles which might damage the columns.
- 3) Column banks must be cleaned on a regular basis.
- 4) A standard asphalt should be run at least once a day. This chromatogram can be used to indicate any malfunction in the system such as leaks or excessive pressure. The most important use of this chromatogram, however, is as a calibration with which other samples run on the same day may be compared. This aspect will be discussed further in Section II, Use of the model asphalt. It should be emphasized at this point, however, that use of such a calibration standard is very common in analytical techniques.

D. Effect of solvents used for mobile phase

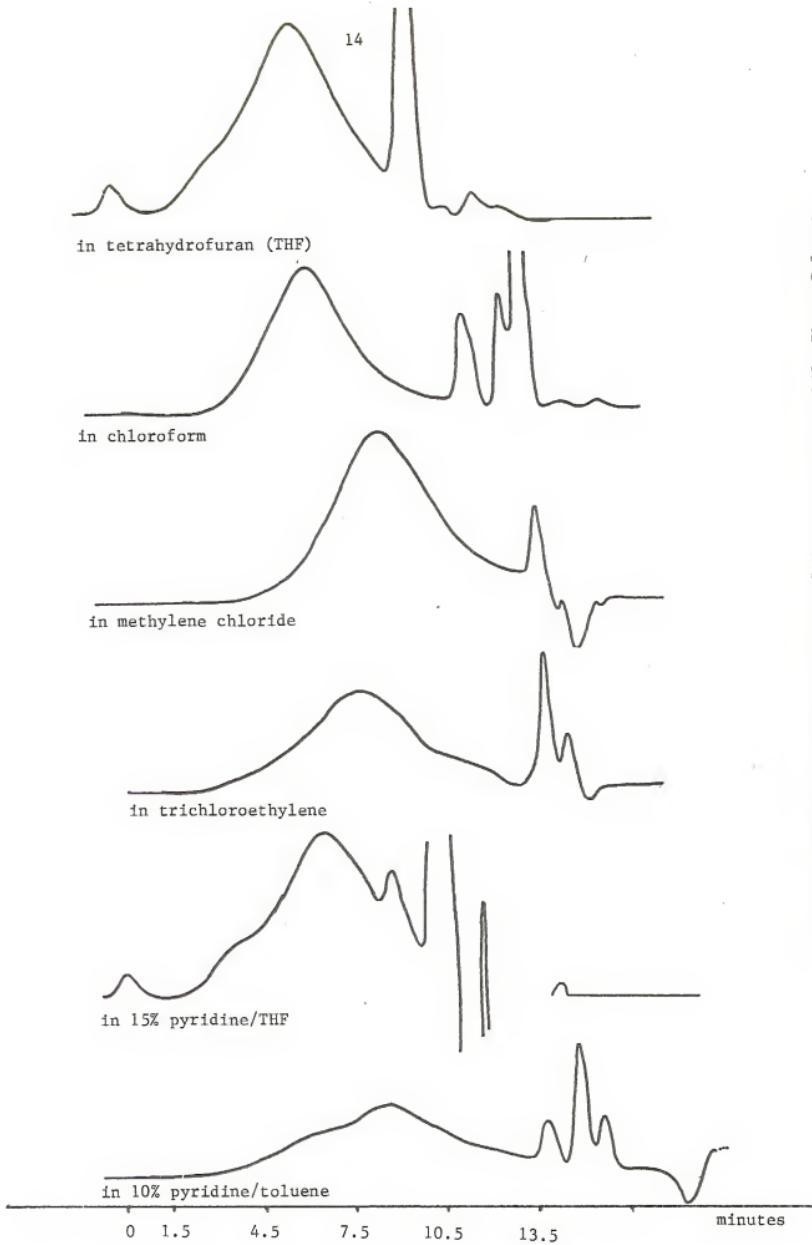
Analyses by high performance gel permeation chromatography are dependent not only upon the columns but also upon the solvent used for the mobile phase. The mobile phase may affect the elution time by modifying the separation method, for example, by superimposing a separation by affinity on the separation by molecular size. The mobile phase may also change the apparent molecular size of sample components by promoting or inhibiting the aggregation of molecules. Change in apparent molecular size may also be seen if the mobile phase causes a change in the swelling of the column packing material which would result in a change in the pore sizes. Such effects, if reproducible, can sometimes be used to good advantage in an analysis.

Several solvents and solvent combinations were selected for testing. Trichloroethylene (TCE), chloroform, methylene chloride, 10% pyridine in toluene and 15% pyridine in THF were used as the mobile phase in the analysis of 4 different asphalts. Results for two of these asphalts are shown in Figures 3 and 4.

Asphalt was soluble in TCE, chloroform and methylene chloride. However, these three solvents contributed to rapid fouling of the HP-GPC columns and would not, therefore, be suitable for general use in this project. However, it is interesting to note in Figures 3 and 4 that all three of these solvents caused an overall increase in retention times of the asphalts. Moreover, the relative order of initial elution time was shifted when compared with chromatograms run in THF. For example, Figure 5 compares the chromatograms of the four asphalts run in THF with those run in chloroform. In THF, asphalt 48 apparently contains the largest molecules followed in order by asphalts 1, 26 and 4. In chloroform, however, the order is 48 > 4 > 1 > 26. This indicates some chemical differences among the asphalts which are not shown by the usual method of analysis in THF.

Pyridine in toluene (1:9) has been suggested as a mobile phase in asphalt analyses run at elevated temperatures (3). However, as can be seen in Figure 6, this combination serves to extend elution time by more than 50% at room temperature. It must be emphasized that separations by size alone in this system will occur during the passage of one column volume of solvent, i.e., within approximately 18 minutes after the elution of the polystyrene standard. Peaks which develop after that time show that some sort of associative mechanism has been superimposed upon the size separation. Therefore, nothing can be said about the size of

Figure 3. HP-GPC Analyses of Asphalt #26-C in Various Mobile Phase Solvents



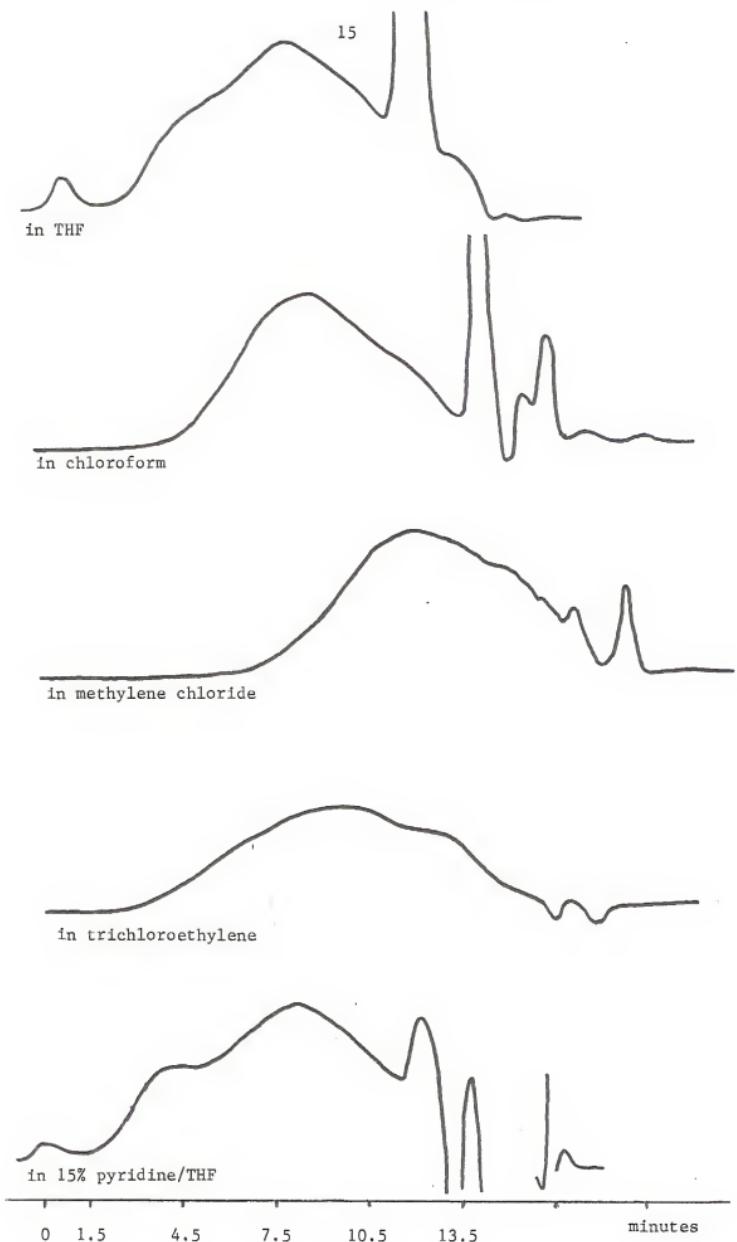


Figure 4. HP-GPC Analyses of Asphalt 1-C in Various Mobile Phase Solvents

Legend

— Asphalt 1

- - - Asphalt 4

· · · · Asphalt 26

— · · Asphalt 48

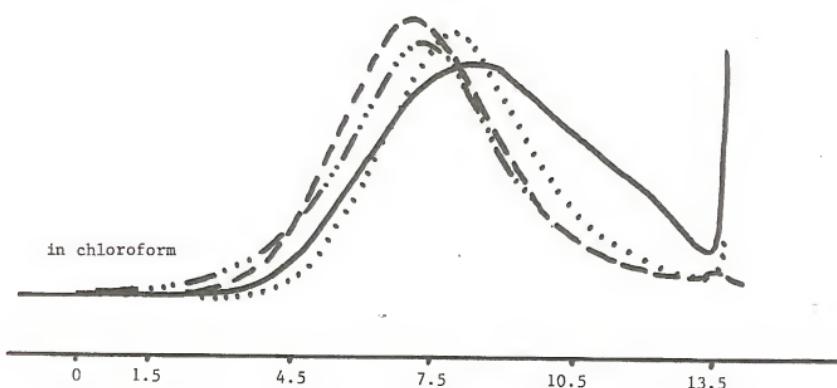
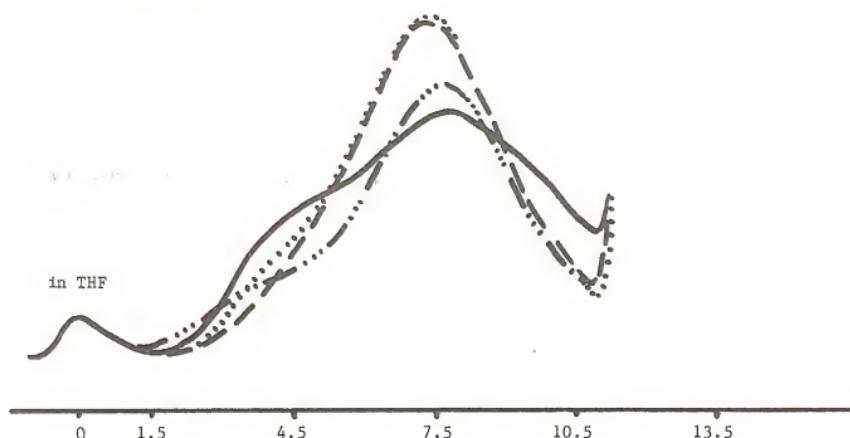


Figure 5. Comparison of Elution Order of Asphalts as Analysed in THF and Chloroform

Legend

Asphalt 48 in THF

Asphalt 48 in 10% pyridine/toluene

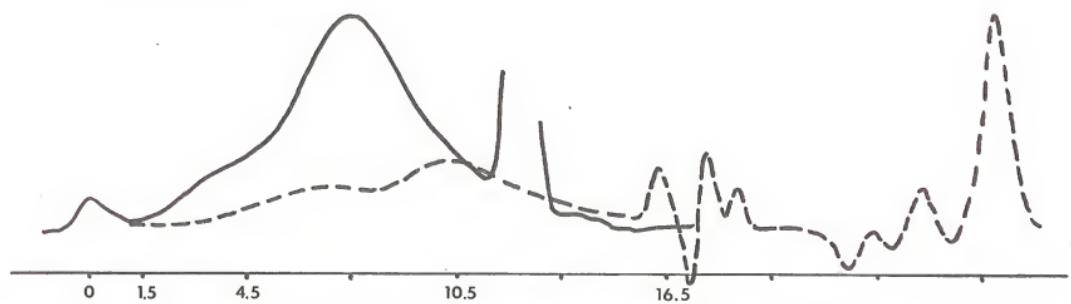


Figure 6. Comparison of Analyses of Asphalt 48 in THF and in 10% Pyridine in Toluene

these materials, only that association caused by pyridine retains them on the columns. Furthermore, this system is not reproducible and it greatly increases the analysis time. Therefore, it is not suitable for purposes of this study. Further work with this system at elevated temperatures might be productive, however.

Pyridine in THF (15:85) can be seen in Figure 7 to enhance the differences between the chromatograms when compared with THF alone. To take advantage of this, the present system would require small adjustments in order to move the internal standard away from overlap with the asphalt. Nonetheless, this mobile phase appears to warrant further examination which time did not permit during this project.

E. Use of UV-vis detector

1) Comparison of UV with RI detection.

It is assumed that some components of asphalt are not detected by the refractive index detector regularly used on this project. This results from the fact that the refractive indices of certain compounds do not differ significantly from the refractive index of THF which is used as the mobile phase. Although no detection system may be expected to be absolutely foolproof, it was felt that the UV detector might offer a slightly different viewpoint for this study. It must be emphasized at the outset that some components of asphalt may be detected by either RI or UV at 254 nm, by both or by neither.

Several experiments were run in which detection at 254 nm was compared with RI. Figure 8 shows typical chromatograms comparing these detectors on one asphalt. It appears that RI is more effective in visualizing material in the LMS and MMS regions but less effective in SMS

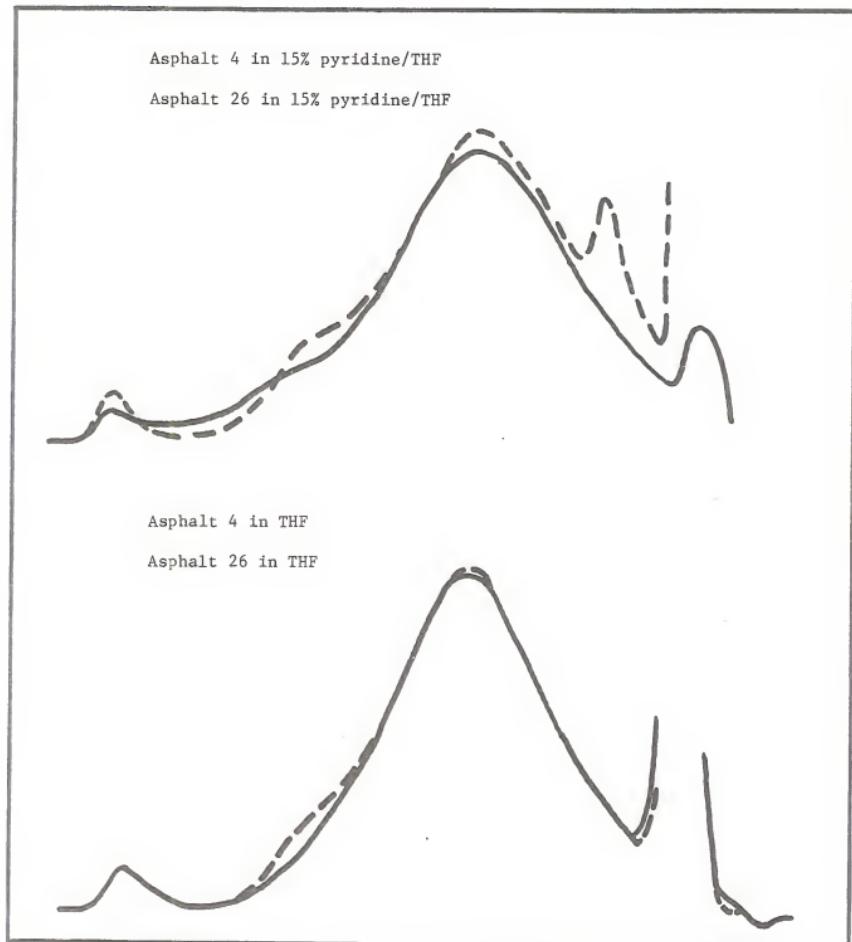


Figure 7. Effects of Added Pyridine on the HP-GPC Analysis of Two Asphalts in THF

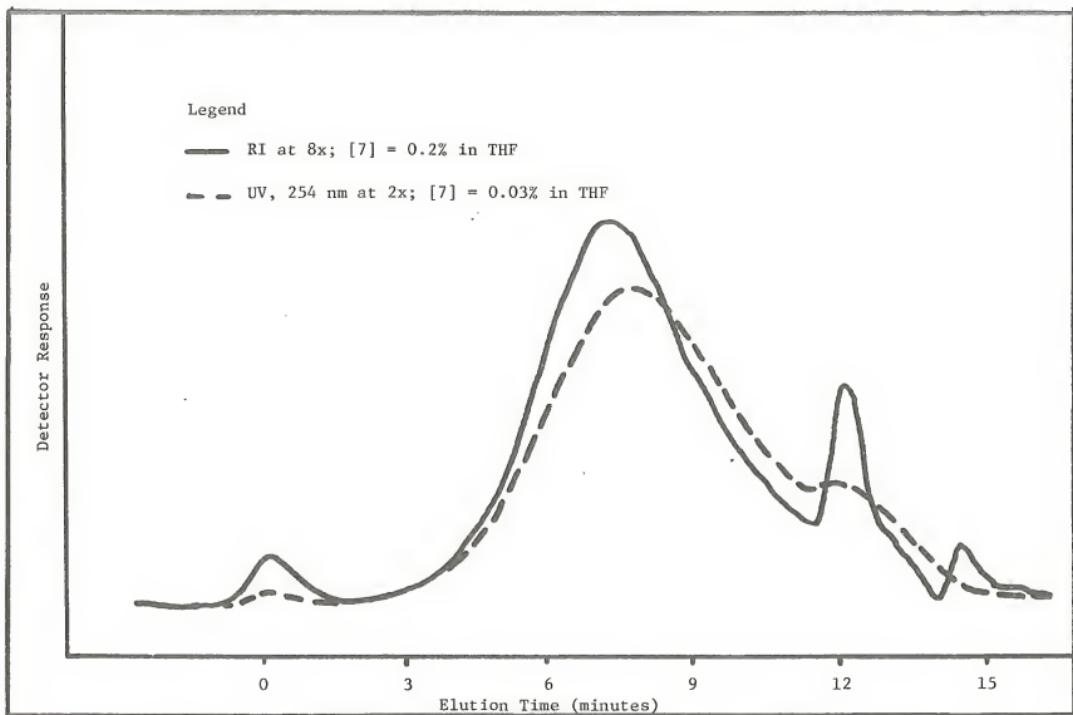


Figure 8. Comparison of UV and RI Detection of Asphalt 7

than is UV. Table 1 compares the area percentages obtained by each detection method for the four asphalts used in this study.

Table 1. Area percentages by RI and UV for study asphalts

Asphalt	RI detector at 8x [asphalt] = 0.2%			UV detector 254 nm, 2x [asphalt] = 0.03%		
	LMS	MMS	SMS	LMS	MMS	SMS
7	7.1	56.0	36.9	6.5	50.9	42.6
34	7.0	56.7	36.3	5.2	50.4	44.4
52	12.5	55.0	32.5	10.1	45.5	44.4
82	8.9	55.2	35.9	5.2	44.9	49.9

Several comments should be made about this data. In all cases, less LMS material is detectable by UV at 254 nm than by RI. This may represent hydrocarbon materials which do not absorb in the UV. These "losses" are not quantifiable at this time but do reflect differences in the molecular composition of these asphalts which are not indicated by RI detection alone.

Similarly, all four asphalts display less MMS material by UV than by RI. This difference ranges from 5 to 10 percent of the whole asphalt.

All four asphalts contain more SMS material detectable by UV than by RI. However, asphalt 82 contains at least 5.5% more UV detectable SMS than any of the other asphalts. Nevertheless, it must be understood that these chromatograms were run under optimum conditions for the detector in question: for RI, sample concentration was 0.2% in THF whereas, for UV, it was only 0.03%. Therefore it was not known whether the differences in molecular size evidenced by the chromatograms in Figure 8 were actually due to differences in detectability of the same components or, rather,

were due to changes in the apparent molecular sizes of the components caused by dilution.

Brief attempts to resolve this dilemma have not achieved satisfactory results, but time was not available on this project for a more serious effort. However, evidence accumulated both here and elsewhere (4, 5)(See Appendix E) indicates that both detectability and dilution are factors in the observed effects. It is likely that some of the materials in the LMS region of the chromatogram (run under the usual conditions for this project) are aggregates of smaller molecules. These aggregates probably dissociate as their concentration in solution decreases, so that less LMS material would be detected by RI as the dilution increased. This was not unexpected. Differences in detectability based on refractive index and UV absorption are also not surprising. Nevertheless, it should be emphasized that the model is based upon the chromatogram of a representative "excellent" asphalt under a given set of conditions, not on any definition of true molecular sizes. Therefore, the validity of the model is not challenged by these findings.

2) Isolation of LMS, MMS and SMS components of an asphalt.

In an attempt to quantify the actual amount of asphalt represented by each of the molecular size fractions, and thereby obtain an indication of the efficiency of the RI detector, an experiment was carried out in which asphalt 112 was separated into its components. Repeated injections of the sample (concentration 0.2%) were made onto the columns. Three fractions were collected corresponding in elution time to the LMS, MMS and SMS regions. Solvent was removed, the samples were redissolved in benzene and rotovapped again to remove all benzene and water and were then weighed. The amounts actually recovered are compared with amounts

detected by RI with asphalt at 0.2% concentration.

	LMS	MMS	SMS
Percent of amount recovered	22.8	40.7	36.5
Percent by area of chromatogram RI, 0.2% concentration	21.0	58.9	20.1

This data indicates that the RI detector reveals about 92% of the LMS components in asphalt 112 but does not detect nearly half of the SMS components. Because this is a percentage calculation, the detector appears then to "see" more MMS material than actually exists.

3) Summary and conclusions for Section E,

Refractive index and UV (254 nm) detectors give varying interpretations of the molecular size distribution of an asphalt depending not only on the mode of detection but also on the concentration of the sample. The following conclusions may be stated:

a. The detection system presently used in this project measures not only the relative size and amount of certain components but probably also measures the ability of certain other components to form larger aggregates.

b. Actual weight percentages of the three HP-GPC fractions of an asphalt show that RI detection ([asphalt] = 0.2%) visualizes about 92% of the LMS material in an asphalt but barely more than half of the SMS components. Because the model asphalt is premised mostly upon the LMS content, the RI detector is still the method of choice.

c. UV detection is the source of some potentially valuable auxiliary information. For example, in Section 1 relative to Table 1, it was stated that asphalt 82 contains about 5.5% more UV-detectable SMS material than the other three test asphalts (at 0.03% concentration).

Extreme care must be exercised in interpreting this data because of the inherent differences between detection systems. Nevertheless, because asphalt 82 was produced by the same refinery which has consistently provided high quality asphalts over the years, these points may warrant further study.

F. Precision

Precision of consecutive analyses of an asphalt on a given day is within 1%.

II. USE OF THE MODEL ASPHALT

In the previous report (2), a model of high quality asphalt for use in Montana was proposed. This model was based on the fact that the best roads existing in Montana (considering age and resistance to cracking) shared a common molecular size profile when analyzed by HP-GPC.

It has since become apparent that a narrowly-defined model profile is not practical at this time. System variables can cause shifts in the MSD of the same asphalt (see section I(C), Column Selection). These shifts are of degree rather than kind. Therefore, the model asphalt is used not only for comparison with other asphalts (eg., in performance prediction) but also for calibration of the HP-GPC system.

As suggested in section I(C), analyzing the model asphalt as the first run of the day can help to detect problems with the system. The model profile for a given day can also be used to determine whether or not direct comparisons of various other chromatograms can be made. If the daily model profiles are alike, the comparisons may safely be made. If not, then comparisons should be made only with caution, or, better, the samples to be compared should be rerun at the same time. This principle will be followed throughout this report. The reader should be aware that different profiles and area percentages for the same sample may appear in this report. This results from the fact that several different column sets have been used during the 18-month course of the project.

The major purpose of the model, of course, is in the prediction of performance of paving asphalts. This use will be discussed more fully in Section VI, but a few points should be stated here.

- 1) Experience has shown that deviations from the model profile by a given asphalt are most serious when the subject asphalt contains more LMS.

2) Tentative limits within which the asphalt being tested should match the model are set as follows:

LMS - within +0% and -2% of value for model

MMS - within +1% and -3% of value for model

SMS - within +3% and -1% of value for model

3) The model applies to finished asphalts

4) The model should be considered for use only in Montana at this time.

These limits are only tentative. They are based on previous experience with asphalts which have performed well in Montana roadways. They also allow for some minor changes which may occur during further aging in the roadway.

III. LABORATORY SIMULATION OF FIELD EFFECTS

In the process of designing an asphaltic pavement, several methods may be used to predict characteristics of the finished pavement. For example, mixtures of the selected aggregate with asphalt of the chosen penetration grade may be subjected to various strength tests. Also, the asphalt may be tested for aging characteristics by the thin film oven test (TFOT). However, since HP-GPC appears to be diagnostic, a laboratory method which will reproduce the effects of mixing and lay-down in the field upon the molecular size distribution (MSD) of the asphalt would have tremendous potential in the study of a variety of parameters associated with product quality. Such a method has been developed and will be the subject of this section.

It will be shown in subsequent sections of this report that the MSD of asphalt in a finished pavement is a function not only of the asphalt itself but also of the aggregate, additives, temperature and exposure time. Therefore, a dependable method of reproducing these effects in the laboratory will be essential to the successful use of HP-GPC as a design tool.

The search for this method involved four 1980 paving projects for which samples of original asphalt cement, the original aggregate and a core taken shortly after construction were available. In the laboratory, mixtures of the aggregates with the corresponding asphalts were prepared and heated at 115°C (240°F). Samples were taken immediately and at 5 minute intervals up to 75 minutes. Identical mixtures were heated at 163°C (325°F) and sampled every 5 minutes for 20 minutes. The resulting mixtures were extracted and the extracts subjected to HP-GPC analysis. Asphalts extracted from the corresponding roadway cores were also

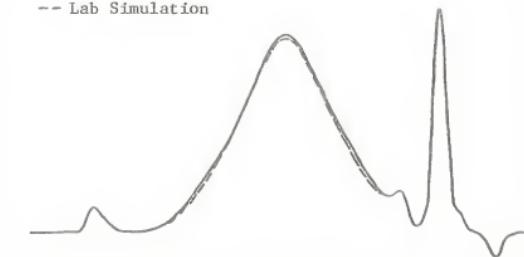
analyzed.

In Figure 9, chromatograms of the asphalts recovered from cores (solid lines) are compared with those from the corresponding laboratory-generated asphalts (dashed lines) sampled after 5 or 10 minutes at 115°C. These pairs of chromatograms coincide well in the LMS region and show small discrepancies in the MMS and SMS areas. These four tests indicate that a laboratory sample prepared as described above and heated at 115°C for 5-10 minutes can be depended upon to give a very close approximation of the MSD to be expected on the roadway. Chromatograms of other samples up to 40 minutes, while not demonstrating such a precise visual "fit" with the field sample, were nevertheless, very close.

Typical area percentage data are presented in Table 3.

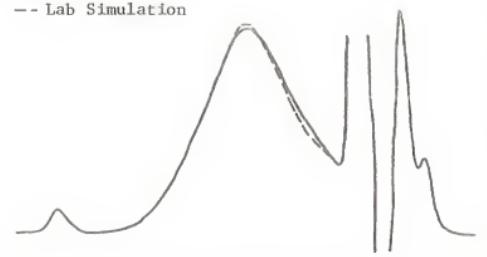
Glasgow - N. W.

— Roadway Core
-- Lab Simulation



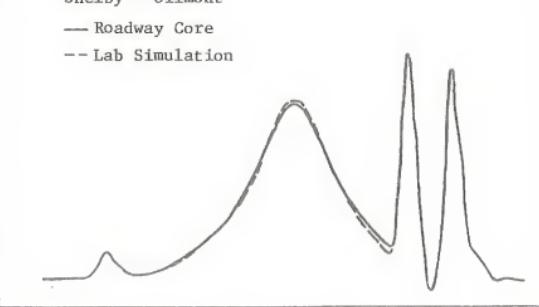
Lodge Grass - No.

— Roadway Core
-- Lab Simulation



Shelby - Oilmont

— Roadway Core
-- Lab Simulation



Half Moon - So.

— Roadway Core
— Lab Simulation

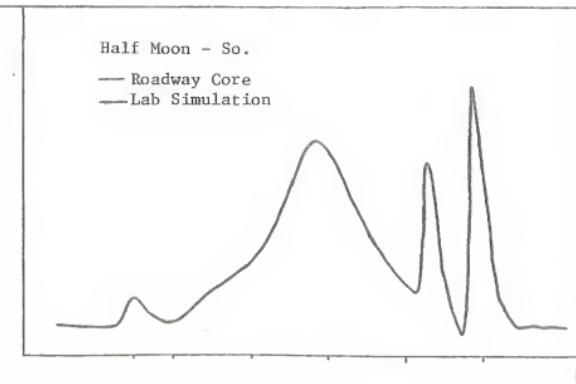


Figure 9. Comparisons of Asphalts From Laboratory Simulated Paving Mixtures With Asphalts From Corresponding Roadway Cores

Table 3. Correlation of field with laboratory samples

A. For Half Moon - South

Sample	Area %		
	LMS	MMS	SMS
Untreated asphalt cement	13.3	53.8	32.9
Pavement core ("field")	14.2	53.1	32.7
Lab mixture - 115°C - 0 hour	14.3	52.8	32.9
5 min.	14.6	52.7	32.7
10 min.	14.5	52.6	32.9
30 min.	14.0	53.8	32.2
35 min.	14.1	53.6	32.3
40 min.	14.7	53.2	32.8
Lab mixture average	14.4 \pm 0.3	53.1 \pm 0.1	32.6 \pm 0.3

B. For Glasgow - NW

Sample	Area %		
	LMS	MMS	SMS
Untreated asphalt cement	5.9	52.8	41.3
Pavement core ("field")	7.4	51.6	41.0
Lab. mixture 115°C - 5 min.	7.4	53.4	39.2
10 min.	7.1	53.4	40.8
20 min.	7.2	52.1	39.5
35 min.	7.7	53.3	38.6
40 min.	7.1	53.5	39.4
Lab mixture - average	7.3 \pm 0.4	53.2 \pm 0.2	39.5 \pm 1.3

Both the chromatograms and the area percentage data show that there appears to be a rapid change in MSD upon contact with heated aggregate (115°C) followed by small fluctuations until about 40 minutes have passed. After that, or at higher temp (eg., 163°C) gradual changes, especially increases in LMS content, occur (Figure 10).

One might theorize that there are indeed no changes in MSD of an asphalt at 115°C between 5 and 40 minutes. If that is so, the small variations within each group must be explained. The variations could result from the sampling method. Because the HP-GPC technique requires only very small amounts of asphalt, about 100 gr. of aggregate and 6 g asphalt were used in these experiments. Efforts were made to obtain representative samples of aggregates. However, the individual timed samples of mixture consisted of, perhaps, only a few pieces of aggregate. Since aggregates are not uniform, this might be expected to contribute to differing MSD's in the asphalt. Increasing the sample size might be expected to decrease this source of variability. However, it would also make the experiments very cumbersome for our facilities. Very small variations in area percentage within a given set of analyses may also result from the process by which the data processing system determines the baseline from which peak area is subsequently calculated.

Considering these factors, the point might not be so much that there is variability in this time frame but rather that the agreement is as good as it is.

Nevertheless, this variability must be dealt with if the method is to be useful for predicting the final MSD of an asphalt in a pavement. In all four cases, the average LMS content of the laboratory-generated samples at 115°C , 5-40 minutes, was within 0.6% of that in the core. The

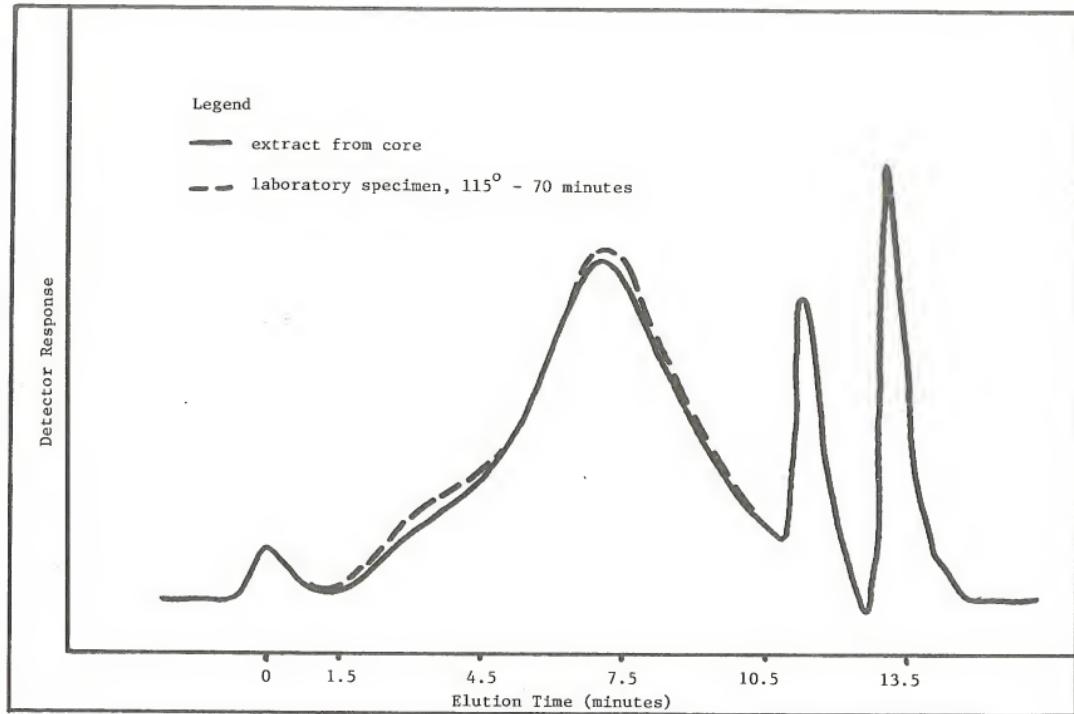


Figure 10. Production of Excess LMS Material After 70 Minutes at 115°C

average MMS values were within 1.6% of the core; average SMS amounts were within 1.5% (Table 4). In three of the four cases, however, the average

Table 4. Comparison of laboratory average area percentages with field area percentages.

Sample	LMS	MMS	SMS	Area %
For Shelby-Oilmont (drum dryer)				
core	10.3	55.1	34.6	
average lab	<u>10.9</u>	<u>53.9</u>	<u>35.1</u>	
difference (lab - field)	+0.6	-1.2	+0.5	
For Lodge Grass - North (batch)				
core	5.8	51.7	42.5	
average lab	<u>5.7</u>	<u>53.0</u>	<u>41.3</u>	
difference (lab - field)	-0.1	+1.3	-1.2	
For Half Moon - South (drum dryer)				
core	14.2	53.1	32.7	
average lab	<u>14.4</u>	<u>53.0</u>	<u>32.6</u>	
difference (lab - field)	+0.2	-0.1	-0.1	
For Glasgow - N.W.				
core	7.4	51.6	41.0	
average lab	<u>7.3</u>	<u>53.2</u>	<u>39.4</u>	
difference (lab - field)	-0.1	+1.6	-1.6	

LMS percentage was within 0.2% of the field sample. It should be noted that the method is no more representative of either the batch plant or drum dryer, at least in this limited sampling.

In conclusion, the data from these four cases shows that the method (Appendix B) can be used to obtain a reliable prediction of the chromatographic profile of an asphalt after processing and lay-down in the field. The method requires that the asphalt and aggregate to be used in the field also be used in the laboratory simulation.

IV. EFFECTS OF HEATING, ADDITIVES AND FILLERS

Evidence accumulated in earlier work for MDOH showed that the LMS percentage of an asphalt increased during processing. It was not known, however, what factor(s) actually caused this increase, eg., heat, contact with aggregate, oxidation, etc. Therefore, a series of experiments was undertaken in which an asphalt from each of Montana's four refineries was heated alone or in contact with various agents, under controlled conditions.

The following asphalts were used in the tests described in this section as well as in other experiments discussed in this report.

Asphalt 7 - 120-150/Refiner A

Asphalt 34 - 120-150/Refiner B

Asphalt 52 - 120-150/Refiner D

Asphalt 82 - 120-150/Refiner C

Samples of asphalt or mixtures of asphalt and agent were heated at 115° (the approximate temperature of the drum dryer) and were sampled immediately ("0" hr), after 0.5 hour and 1 hour. Identical samples were heated at 163°C (the temperature used in the thin film oven test). The asphalts were extracted and analyzed according to standard procedures. (Complete procedures are described in Appendices C and D.) Data derived from these experiments will be discussed according to the agent involved in the next paragraphs (A - H) and summarized in section IV-J.

A. Heat

In order to determine the effects of heat, alone, on the molecular size distribution of an asphalt, sets of samples were heated at these temperatures under ambient atmosphere, with additional air blown into the

oven and with nitrogen blanketing the samples. These samples were not treated as extremely thin films. A total of 72 samples were prepared and analyzed. Heating each of the sample asphalts under ambient atmosphere caused negligible changes in the molecular size distribution. Under nitrogen, samples 52-0 (Refiner D) and 7-0 (Refiner A) showed small increases in LMS in the 115° - 0.5 and 1 hour samples. These changes were somewhat stronger than those which occurred in ambient atmosphere but still were very small. With additional air supplied, the changes with time and temperature were also very small and no trends were exhibited.

In summary, heating of asphalts from all four refineries in ambient atmosphere, under nitrogen or with additional air causes no significant changes in the molecular size distributions of the asphalts. Therefore, some other factor or combination of factors must lead to the changes observed in field samples.

B. Aggregates

The search for the causes of changes in molecular size distribution of asphalts brought about during processing included experiments in which the four test asphalts were heated in the presence of each of five aggregates (labelled A, B, C, D and E). The aggregates were selected by MDOH to represent "good", "fair", and "poor" classes. Petrographic analyses are included in Appendix G.

Sample mixtures consisting of aggregate and 6% asphalt (by weight of aggregate) were heated under ambient atmosphere as described above.

An example of data derived from these experiments is given in Figure 11. This set of chromatograms illustrates the effect on asphalt 52 (Refiner D) of heating with aggregate A. Several points will be made

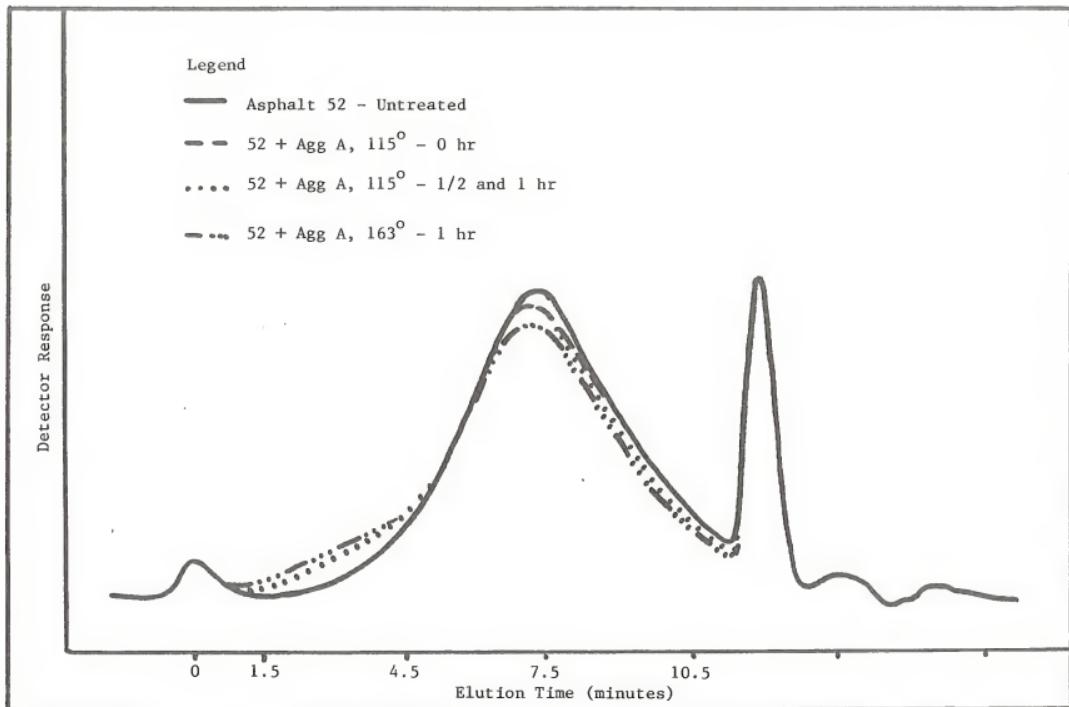


Figure 11. Effect on Asphalt 52 of Heating in the Presence of Agg A

about this example. Subsequently, the relationship of other asphalt-aggregate combinations to this example will be discussed.

1) The chromatograms for asphalt 52 - untreated and for the sample taken at 115° - 0 hr. (i.e., immediately after mixing with aggregate at 115°C) show that there was an immediate, albeit small, change in the molecular size distribution (MSD) of the asphalt on contact with heated aggregate. That change is evidenced by the drop in peak height of the 115° - 0 hr. sample which results in a larger percentage of LMS material.

2) A larger increase in the amount of LMS material occurred upon continued heating at 115° for 0.5 or 1 hour. As explained in Section III, the 115° - 0.5 hr. chromatogram approximates the likely outcome of processing and lay-down of this particular asphalt-aggregate combination on a roadway.

3) The chromatogram for the 163° - 0 hr. sample was omitted from Figure 11 for the sake of simplicity. However, it shows an amount of LMS material greater than the 115° - 0 hr. but less than the 115° - 0.5 and 1 hour samples.

4) Continued heating of the mixture at 163°C for 0.5 to 1 hour caused greater increases in amount of LMS than did similar exposures at 115°C.

These four points are generally applicable to the other asphalt-aggregate combinations studied. For example, all of the asphalts underwent immediate changes in MSD upon contact with heated aggregate (115°C). However, aggregate B caused this effect in only one of the four asphalts.

Furthermore, in 80% of the mixtures tested, the 115° - 0.5 hr. sample contained more LMS material than the 115° - 0 hr. sample. The

other cases contained about the same amount of LMS; in no case was there less LMS material in the 0.5 and 1 hour samples than in the 115° - 0 hour samples.

In about one-half of the mixtures, the 163° - 0 hr. sample showed smaller amounts of LMS material than in 115° - 1 hr. samples.

For three of the four asphalts tested, heating with aggregate at 163° for 0.5 to 1 hour produced more LMS material than did heating at 115°C. Only asphalt 34 (Refiner B) did not follow that pattern. Nonetheless, these larger increases in LMS content at higher temperatures and/or longer exposure times in the laboratory appear not to be indicative of the changes which occur during the normal road building situation. They should, however, serve as harbingers of the potential effects of changes in "normal" construction procedures.

Area percentage data which should most closely approximate the effects of processing and construction for these asphalt-aggregate mixtures are given in Table 5. The increases in LMS content of these

Table 5. Effects of heating with aggregate on percentage of LMS

Treatment/Aggregate	Asphalt and Source							
	7 Refinery A		34 Refinery B		52 Refinery D		82 Refinery C	
	% LMS	Diff*	% LMS	Diff*	% LMS	Diff*	% LMS	Diff*
Untreated	6.5		7.0		8.7		8.3	
115° - 0.5 hr with A	7.7	+1.2	7.3	+0.3	12.6	+3.9	9.5	+1.2
Untreated	6.5		7.0		8.7		8.3	
115° - 0.5 hr with B	7.4	+0.9	8.3	+1.3	11.2	+2.5	8.6	+0.3
Untreated	7.0		7.0				8.3	
115° - 0.5 hr with C	8.3	+1.3	9.7	+2.7			8.5	+0.2
Untreated	7.0		7.0		8.7		8.3	
115° - 0.5 hr with D	8.0	+1.0	7.0	+0	10.9	+2.2	9.0	+0.7
Untreated	7.0		7.0		8.7		8.3	
115° - 0.5 hr with E	9.4	+2.4	8.1	+1.1	11.3	+2.6	8.4	+0.1

*Difference = (% LMS in 115° - 0.5 hr) - (% LMS in untreated asphalt)

asphalts after 0.5 hour in contact with the aggregates at 115°C range from negligible to 3.9%. Overall, asphalt 82 appears to be the least susceptible to change in LMS content under these conditions. The largest increase for asphalt 82 was 1.2%. Asphalt 52 is, generally, the most susceptible with increases ranging from 1.6 to 3.9%. Interestingly, in five construction projects monitored during 1981, a similar, rather wide range of differences between the LMS content of the untreated asphalt and of the corresponding asphalt from a finished core was seen. The smallest increase was 0.7% (asphalt from Refinery C); the largest was 4.7% (Refinery B). (See Section VI.)

In summary, contact with aggregate at 115°C and 163°C has been shown

to cause immediate changes in the MSD of asphalts. These changes, particularly an increase in the amount of LMS material present in an asphalt, generally increase with time and temperature. Certain asphalts appear to be less susceptible to the LMS increase than others, especially at 115° - 0.5 hour. Under these conditions the response to contact with aggregate appears to be primarily asphalt dependent. However, the range of responses seen in these experiments and in recent field data makes the prediction of final LMS content based solely upon the LMS percentage of the untreated asphalt difficult at best. However, by using the procedure outlined in Section III, the final LMS content can be determined.

C. Hydrated Lime

Hydrated lime is sometimes added to paving mixes to improve the performance of the mixes in tests for adhesion, immersion compression and volume swell. Earlier work (2) had indicated that lime might be responsible for larger increases in LMS content during processing than those brought about by aggregate alone. To test the effects of lime in the laboratory, a series of experiments involving heating mixtures of the test asphalts and aggregates with lime were undertaken. Unfortunately, HP-GPC analysis of a series of many samples containing lime caused excessive pressure to build up in the system. (This is a cumulative effect seen when analyzing a lengthy series of samples; it should not be a deterrent to the occasional analysis of small sets of lime-containing asphalts.) Therefore, all of the samples prepared were not analyzed. However, data from those that were analyzed are instructive.

For example, heating an asphalt with lime alone was shown to cause an increase in LMS content (Table 6).

Table 6. Effect of lime on LMS content of asphalt 7

Sample	% LMS
7 - Untreated	7.0
7 + lime, 115° - 0 hr	8.1
7 + lime, 115° - 0.5 hr	9.4

The effect of lime on the mixtures of asphalt 82 with aggregates is particularly striking. Area percentage data is presented in Table 7. This asphalt from refiner C appeared to be less susceptible

Table 7. Effect on LMS: Aggregate vs. aggregate plus lime at 115°C - 0.5 hr

Sample	Difference in % LMS*	
	82 + Aggregates	82 + Aggregates + Lime
Aggregate A	+1.2	+4.2
Aggregate B	+0.3	+5.0
Aggregate C	+0.2	+5.9
Aggregate D	+0.7	+4.6

*Difference = (% LMS in 115° - 0.5 hr) - (% LMS in untreated asphalt)

than other test asphalts to LMS increase caused by heating with aggregates (Section IV-B). However, with addition of lime, the tendency for LMS material to accumulate is very strong. Moreover, when asphalt 82 and aggregate A, for example, were heated at 115°C for 0.5 hour, the resulting asphalt still was within range of the model. Under the same

conditions but with lime added, the asphalt exceeds the model (Figure 12).

Although data for the other asphalts is not complete, these asphalts appear to be somewhat less affected by the addition of lime than asphalt 82. There is no evidence that the addition of lime ever results in a decrease in LMS content. As with aggregate alone, the final MSD of an asphalt mixed with aggregate and lime may be predicted by use of the procedure for laboratory simulation of field effects. In view of the results with asphalt 82 discussed above, the potential effect of lime should not be ignored.

D. Fly ash

Fly ash is frequently used in the construction of asphaltic pavements as a filler. To elucidate the effects of fly ash, mixtures were prepared using the same four asphalts and five aggregates plus 1.5% fly ash (by weight of aggregate). These mixtures were heated at the temperatures and times outlined at the beginning of Section IV.

A set of chromatograms which typifies the results is shown in Figure 13. As with aggregate alone, there is a general increase in percent of LMS with time. However, in most cases, not only is the increase greater when fly ash is added, but also the change occurs more rapidly. That is, the LMS content undergoes a larger increase as soon as the asphalt contacts the heated aggregate-fly ash mixture. This is demonstrated by examples in Table 8.

Legend

— Asphalt 82 + Agg A, 115° C, 1/2 hr

-- Model

(chromatograms run 1/2/81)



Legend

— Asphalt 82 + Agg A + lime, 115° C, 1/2 hr

-- Model

(chromatograms run
12/30/81)

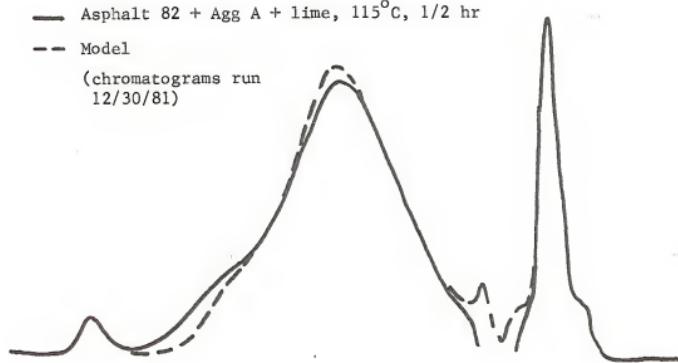


Figure 12. The Effect of Lime on the Ability of an Asphalt to Match the Model

Table 8. Effects on LMS: aggregate vs. aggregate plus fly ash at 115°C - 0 hr

Asphalt	Differences in % LMS*	
	Aggregate A	Aggregate A + fly ash
7	0.4	1.6
34	0	3.9
52	-0.8	3.8
82	0.7	2.5

*Difference = (% LMS in 115° - 0 hr) - (% LMS in untreated asphalt)

In Table 9, data are presented which compare the effects of aggregate at 115°C - 0.5 hr with those of aggregate and fly ash under the same conditions. It can be seen that, in most cases, more LMS is formed when

Table 9. Effects on LMS: aggregate vs. aggregate plus fly ash
at 115° - 0.5 hr

Aggregate	Differences in % LMS*							
	Asphalt 7		Asphalt 34		Asphalt 52		Asphalt 82	
A	Agg 1.2	Agg + FA 2.4	Agg 0.3	Agg + FA 3.1	Agg 3.9	Agg + FA 4.0	Agg 1.2	Agg + FA 3.4
B	0.9	0.1	1.3	5.7	2.5	5.0	0.3	3.3
C	1.3	4.1	1.7	5.3	1.6	2.9	-	-
D	1.0	0.7	3.9	4.7	2.2	2.0	-	-
E	2.4	3.2	1.1	2.1	2.6	0.4	0.1	3.3

*Difference = (% LMS in 115° - 0.5 hr) - (% LMS in untreated asphalt)

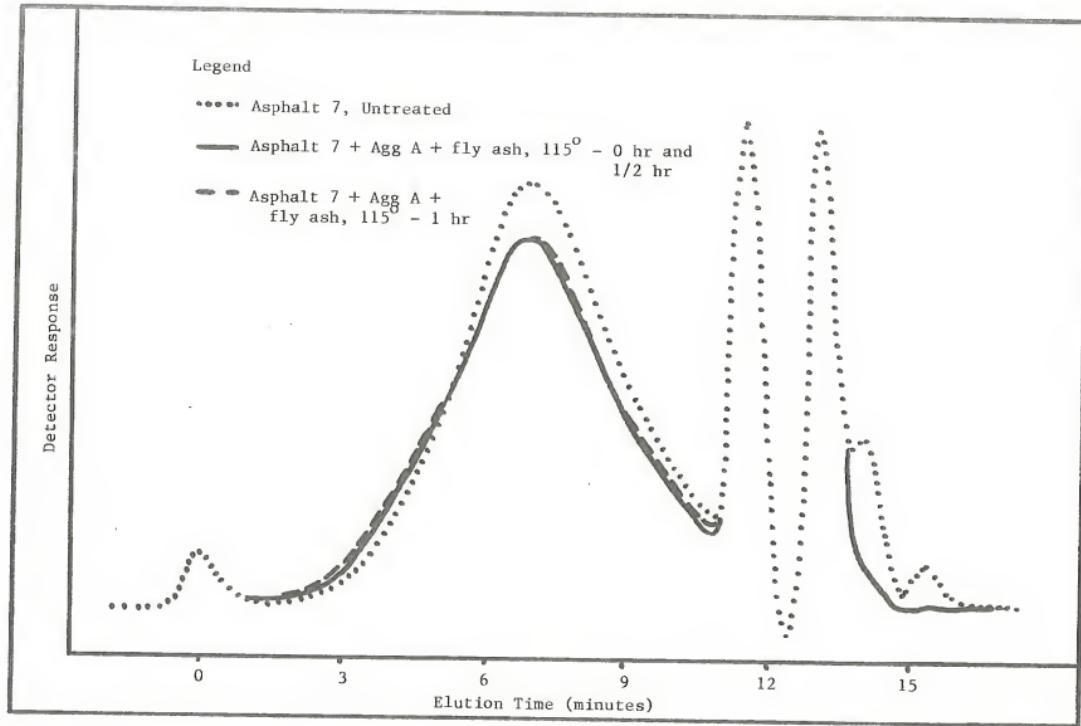


Figure 13. Effect of Fly Ash on the Molecular Size Distribution of Asphalt 7 With Aggregate A

fly ash is included in the mix than when aggregate alone is used. Fly ash can result in the formation of as much as 4.4% more LMS material than the addition of aggregate alone and should not, therefore, be ignored in the design process.

E. Antistripping Agents

Under some conditions, asphalt cement may not adhere well to aggregate and the roadway may succumb to a condition known as stripping. Lime or some other additive - an antistripping agent - may be prescribed to improve adhesion. Many antistripping agents have been patented and are commercially available. During this study, four of these agents, one of which has been used by MDOH, were tested in experimental mixtures with asphalts and aggregates.

Figure 14 shows chromatograms of the four antistripping agents (AsA) which were analyzed under the usual conditions for analysis of asphalt. The areas of the chromatograms are small, indicating that many components are not detected by refractive index differential. Nevertheless, the components which are visualized differ among the agents tested. AsA-1 and AsA-2 appear to share components of similar molecular size but in different amounts.

In this research, no attempt was made to ascertain the ability of these products to carry on their intended function, i.e., to improve adhesion. Instead, the objective was to determine what effects, if any, these antistripping agents have on the molecular size distribution of an asphalt. Examples of the data obtained are given in Table 10.

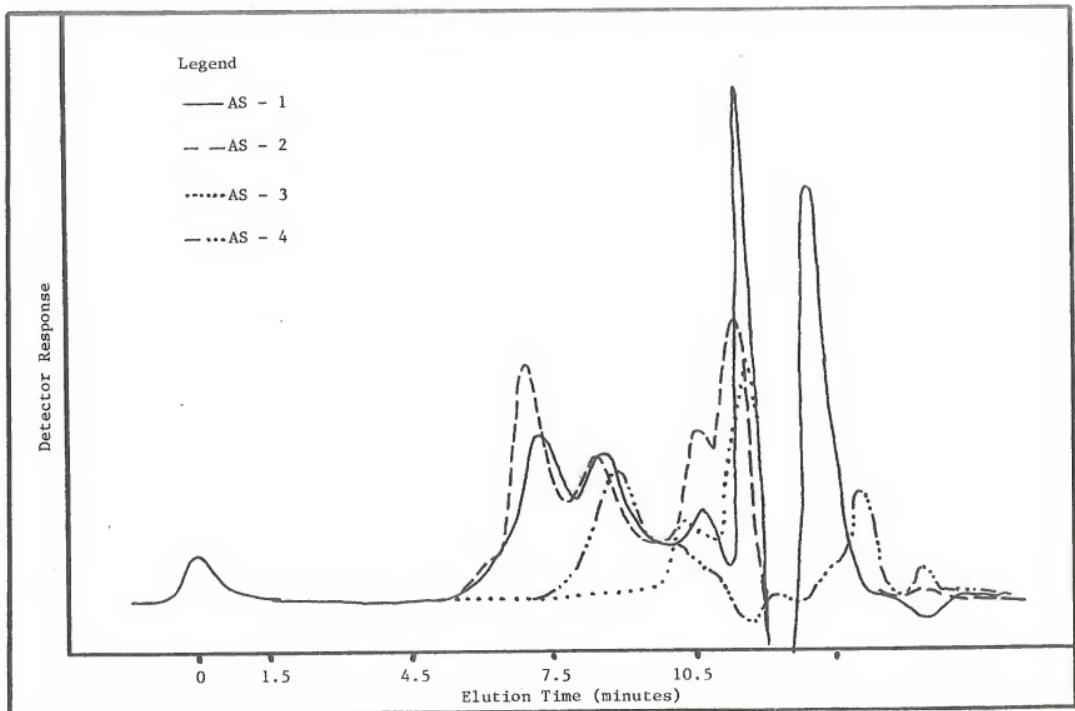


Figure 14. HP-GPC Chromatograms of Antistripping Agents

Table 10. Effect on LMS: aggregate vs. aggregate plus antistripping agents (AsA) at 115°C - 0.5 hr:

Antistripping Agent	Difference in %LMS*			
	Asphalt 34		Asphalt 52	
	Agg A	Agg E	Agg A	Agg E
None	0.3	1.1	3.9	2.6
AsA-1	2.8	2.5	3.6	1.2
AsA-2	3.5	4.4	3.7	1.1
AsA-3	2.1	1.3	2.9	1.5
AsA-4	1.9	2.4	1.0	2.3

*Difference = (% LMS in 115° - 0.5 hr) - (% LMS in untreated asphalt)

All of the antistripping agents tested increase the amount of LMS formed in asphalt 34 when compared to aggregate alone. AsA-1 and AsA-2 have the strongest effect in this regard, especially with aggregate A. In general, such an effect would not be desired. However, in this case, the asphalt does not exceed the model in spite of the effect of added antistripping agent (Figure 15).

Asphalt 52 behaves differently in the presence of the antistripping agents. With AsA-1 or AsA-2, and aggregate A, the increase in percentage of LMS material is about the same as with aggregate alone. However, with AsA-3 and, especially, AsA-4, the increase in LMS is not as great. AsA-4 appears to limit the amount of increase to only 25% of that seen with aggregate alone. Unfortunately, asphalt 52 still exceeds the model under these conditions, but to a much lesser extent.

When asphalt 52 and aggregate E form the mixture, the addition of 3

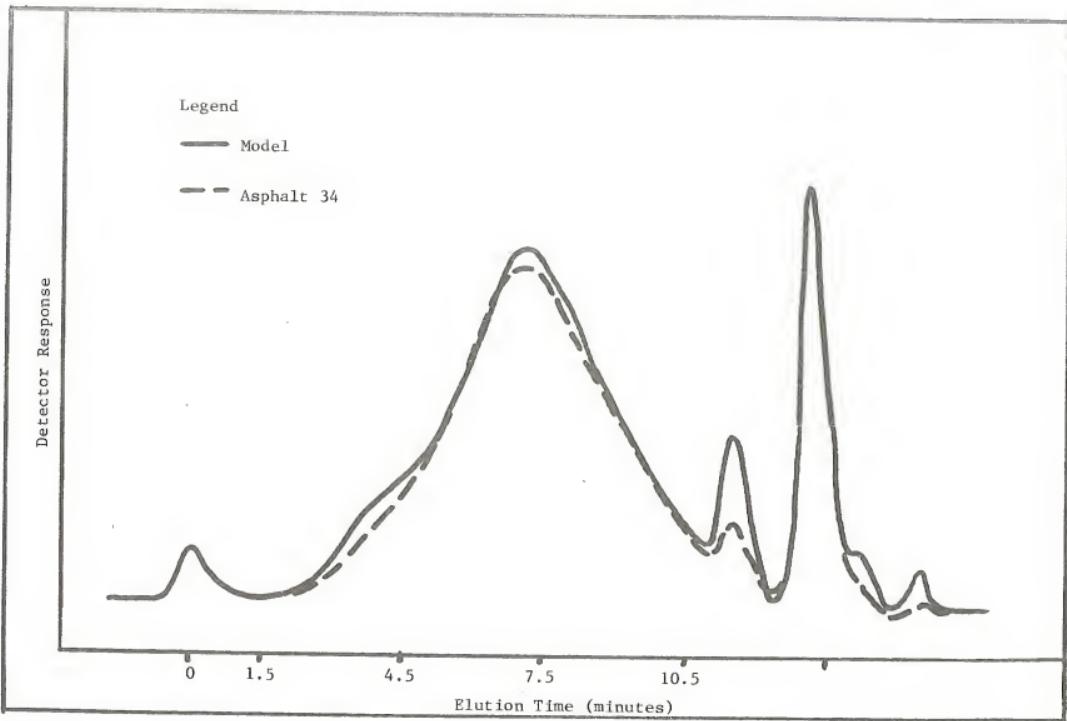


Figure 15. Comparison of Asphalt 34 (at 115° - 1/2 hr With Aggregate A and As - 1) With the Model

of the 4 antistripping agents appear to prevent much of the increase in LMS content caused by aggregate alone.

In summary, antistripping agents should be considered not only for their primary use, i.e., preventing stripping, but also for their effect on the molecular size distribution of the asphalt. The latter effect can be either detrimental or helpful in terms of LMS content, depending upon the asphalt, the aggregate and the antistripping agent; it may be predicted in the laboratory.

F. Sulfur

Sulfur is being used as an extender for asphaltic pavements in some circumstances. Purposes for using sulfur include: the potential for using less asphalt cement than would normally be required in a pavement; making use of large amounts of sulfur which are available in some regions; improving the performance characteristics of the asphaltic pavement (6).

One sulfur-asphalt pavement has been constructed in Montana. Samples of the sulfur-asphalt binder (40:60) and of the plant mix were obtained for HP-GPC analysis. Chromatograms of the asphalts obtained from these samples are shown in Figure 16. The model run on the same day is included for comparison.

Several problems were encountered in the analysis of the samples. First, sulfur is slightly soluble in THF. Moreover, the sulfur is very finely divided and is not easily stripped of asphalt and removed by filtration. The latter fact caused serious difficulties with the HP-GPC apparatus. Severe pressure increases were observed when analyzing these samples. Furthermore, anomalous fluctuations in baseline negate the value of area percentage data.

Nevertheless, some information may be gleaned from the chromatograms

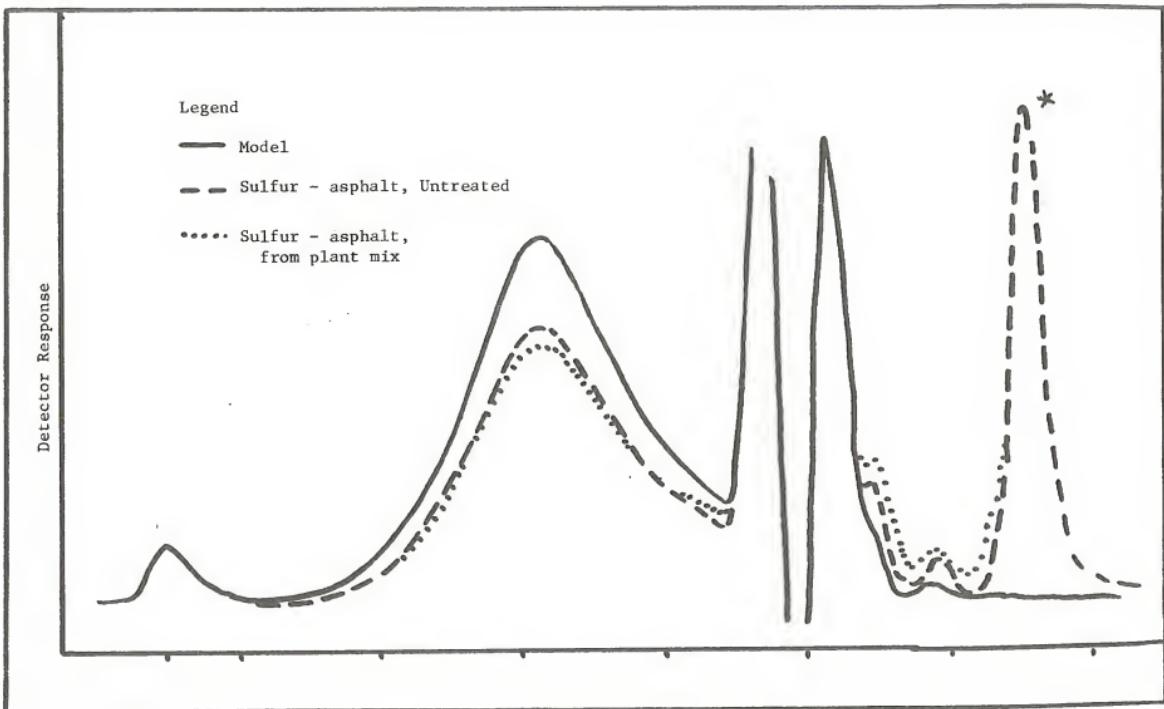


Figure 16. Comparison of Asphalt From Sulfur - Asphalt With the Model

in Figure 16. First, only very small differences are evident between the asphalt from the asphalt-sulfur blend and the asphalt extracted from the plant mix. This indicates that processing with sulfur does not greatly affect the molecular size distribution of this asphalt.

A sharp spike at the far right of the chromatogram (*) appears in the sulfur-exposed samples. Material from this peak was collected and analyzed by mass spectroscopy. Elemental sulfur was identified. Because of the extended retention time, it is clearly displaying an affinity for the column packing material.

Considering the severe difficulties encountered in analyzing these sulfur-containing samples, it must be concluded that HP-GPC is not the optimum method for studying these materials.

G. Rubber

Rubber is being used in some areas as an additive to asphalt paving mixtures. This use provides an outlet for the millions of rubber tires which are discarded in this country. The advantages to the roadway which are said to accrue from the addition of rubber include skid resistance, de-icing characteristics due to flexibility of the pavement, and cracking resistance. Processes by which rubber is added to asphalt paving mixtures have been patented by several companies (7).

Rubber is believed to react chemically with asphalt under some conditions. Because rubber is not very soluble in THF, the rubber is not available for analysis by the present HP-GPC system. Any components of the asphalt which have reacted with the rubber particles are therefore, also not available for analysis. The chromatogram of an asphalt which was extracted from a rubber-asphalt mixture is shown in Figure 17. The chromatogram of the model is included for reference. The extractable

asphalt contains 47.0% SMS material (37.2% in the model) and 43.6% MMS components (54.1% in the model).

As with other additives, HP-GPC can demonstrate what happens to the extractable asphalt in an asphalt-rubber mixture. However, the primary effect of the rubber will be on rheological properties. These properties reflect the total mixture and analysis of the asphalt alone may not be instructive. Further studies of a wider variety of asphalt-rubber pavements by a modified HP-GPC system or some other system are warranted as more examples of rubberized pavements become available for testing and observation.

H. Carbon Black

Carbon black is being offered as a reinforcing agent for asphalt paving mixtures. This agent is said to improve asphalt durability, resistance to wear and temperature-viscosity susceptibility (8). As with other agents considered during this project, the goal was not to test the ability of carbon black to fulfill its intended purpose but rather to determine its effects on the MSD of the asphalt with which it is mixed.

Mixtures of carbon black with each of two asphalts were prepared and heated at 115°C. Samples were taken every 5 minutes. Examples of data are given in Table 11. Heating with carbon black causes some changes in the molecular size distribution of the asphalt, specifically, increases in LMS content. The changes are not large (< 1.8%) but should be expected to be modified by the aggregate which is included in the paving mix.

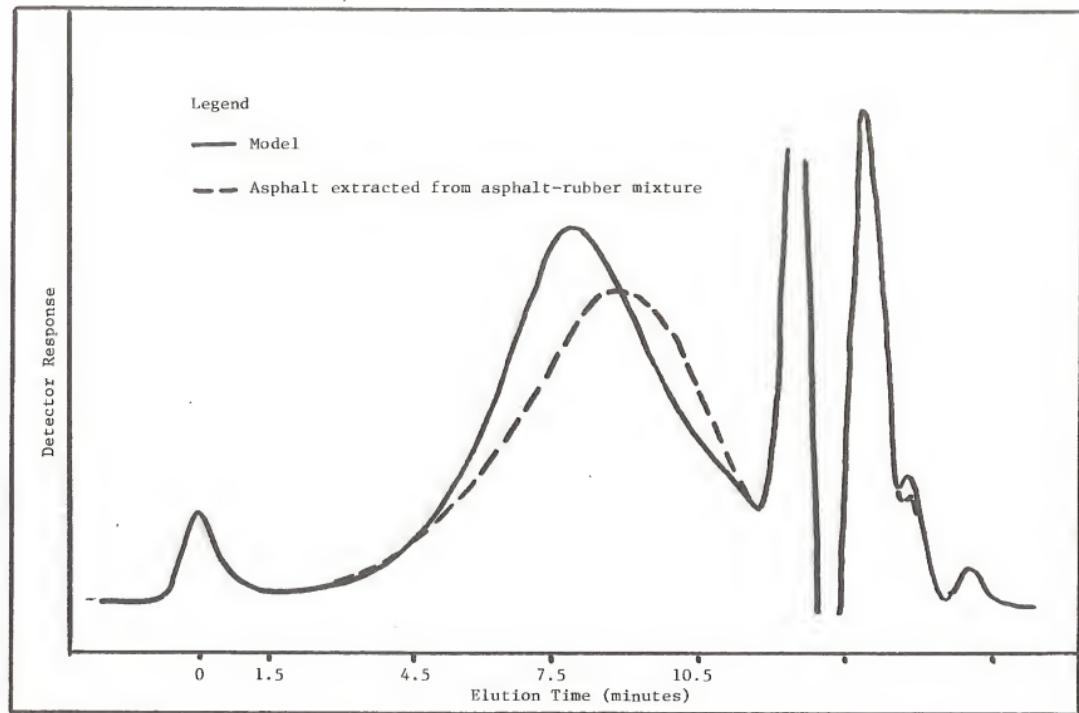


Figure 17. HP-GPC Chromatogram of Asphalt Extracted From a Rubber-Asphalt Mixture

Table 11. Effect on LMS: Heating in the presence of carbon black

	Difference in % LMS*	
	Asphalt 34	Asphalt 52
115°C - 5 min	+0.7	+1.8
115°C - 10 min	-	+1.4
115°C - 15 min	+1.7	+1.6

Difference = (% LMS in treated sample) - (% LMS in untreated asphalt)

J. Summary of Section IV

A number of materials may be added to asphalt in the course of construction of an asphalt pavement. The first of these is aggregate. Other materials may be required to correct deficiencies perceived in the asphalt-aggregate mixture. For example, lime or fly ash may be added to improve results of the immersion-compression test, an antistripping agent may be required to improve the stripping character of an aggregate-asphalt mixture, etc. Such materials may well accomplish their intended purposes, but their effects on the asphalt itself have not been considered.

The extensive series of experiments conducted here involved combinations of four asphalts with five aggregates and other common agents, including hydrated lime, fly ash and antistripping agents. Conclusions which may be reached from these experiments will be enumerated below.

- 1) Heating asphalt alone in the presence of air or nitrogen caused very small if any changes in the molecular size distribution of asphalts.
- 2) Heating asphalts in the presence of aggregates at 115° - 0.5 hr

(the conditions which simulate the effects of processing and lay-down on a roadway) generally caused increases in LMS content of the asphalts. In no case did the LMS content decrease. The increases ranged from negligible to 3.9%.

3) Heating asphalt-aggregate mixtures with lime or fly ash generally caused even larger amounts of LMS to form than with aggregate alone. The additional amounts ranged as high as 4.4%.

4) The effects of addition of the four antistripping agents are variable. In some cases the amount of LMS increase caused by aggregate is enhanced by the addition of antistripping agent but in a few striking cases, the usual increase in LMS is nearly prevented by a specific agent.

5) The effects of all of these materials are complicated and interdependent. Virtually any treatment with one of these agents results in an increase of LMS content. Addition of a second agent results in still further complications, sometimes further increasing the amount of LMS material, sometimes preventing part of the increase caused by another agent.

6) In some cases, an agent changes the MSD to such an extent that the asphalt can no longer match the model.

7) The evidence summarized above demands that the effects of these agents on the MSD of asphalt not be ignored in the design process. The fact that these effects cannot be precisely predicted solely on the basis of the LMS content of the virgin asphalt with present knowledge would appear to make this need difficult to satisfy. On the other hand, the fact that there are so many variations depending on the choice of aggregate, asphalt and agent opens wide the opportunity for engineering the asphalt to match the model. Fortunately, the method outlined in

Section III makes it possible to determine in the laboratory the best available combination of asphalt, aggregate and other agent to satisfy a specific need.

V. AGING OF ASPHALTS IN PAVEMENTS

Aging of asphaltic pavements has long been a concern of highway department officials. Values from typical physical tests are known to change with time. For example, penetration values decrease, a condition known as "age hardening". The effects of long-term aging on the molecular size profile of asphalts was not known because samples of the original asphalt cements and cores taken immediately after construction of the pavements were not available. (Other workers (9 - see Appendix F) have studied asphalts after 4 and 24 months by GPC.) Removal of this uncertainty will permit better definition of the model of high quality asphalt for Montana.

In order to determine the effects of aging on MSD of asphalts, a number of Montana roadways are now available for study, that is, samples of the original asphalt cement and cores taken immediately after construction are on hand. The performance of these roads is also being monitored (see section VI).

Some of the older roads have now been sampled about 2 years after construction. Area percentage data for these roads is presented in Table 12. Values in column A show the change in LMS that results from processing and lay-down. These increases range from 2.1 to 4.0 percent and are, by now, familiar. Column B, on the other hand, shows the changes that have occurred in the LMS content of these asphalts in approximately two years of aging. (A positive number indicates an increase in LMS with time.)

Only one of these examples shows an increase in LMS with time, and that is a very small increase. Three of the roads demonstrate decreases

Table 12. Aging of 1977-78 Pavements

Project #	Termini	Const. Date	LMS %			Difference in LMS	
			original asphalt	core at construction	~2 year core	A*	B**
4	Big Sandy-Rudyard	1978	4.8	7.5‡	7.3‡	+2.7	-0.2
52	Two Medicine Br-E	1978	11.2	13.3	13.9	+2.1	+0.6
43	Sidney-Culbertson-1	1978	6.5	10.5	9.8	+4.0	-0.7
57	Wolf Point-SE-1	1978	7.6	10.6 ^d	8.1 ^d	+3.0	-2.5
7	Bozeman Pass E(East)	1977		15.5	13.3		-2.2
97	Big Sky	1977	6.5	10.5‡	9.5‡	+4.0	-1.0

‡ with lime d with fly ash

* Difference = (%LMS in core at time of construction) - (%LMS in original asphalt cement)

** Difference = (%LMS in core ~2 years old) - (%LMS in core at construction). Positive number indicates increase in LMS with time.

of 1% or less. The remaining two examples show decreases of 2.2 and 2.5 percent. It would not be expected that decreases of this extent would continue as the asphalts age. However, the data are encouraging in that they show no strong trends to increase LMS percentage with time over the first two years of a project. That is, it appears that the initial changes in MSD brought on by processing are the major, if not the only changes which occur in an asphalt pavement.

This information has important implications with regard to the model asphalt. As explained in Section II, the model asphalt is representative of Montana's best roads. These asphalts are 14 to 20 years old. In defining the model, it has been assumed that the MSD of an asphalt does not change significantly after construction. That is, the model is valid for comparison with asphalt from pavement of any age. If the trends indicated by this preliminary data are found to continue as this study progresses, these assumptions will be proved correct.

The contrast between the results from physical tests on aged asphalts and the results from HP-GPC data presented here are perplexing. The "disappearance" of light-end material in the asphalt has been suggested as the cause of penetration decreases with age. However, such changes are not evident in chromatograms. If loss of light-end material does occur, it could be from the SMS material which is not detected by refractive index differential (See Section I-E). These materials are likely to be small hydrocarbons (<10 C-atoms). Some method of detection for these SMS materials might shed some light on the mechanism of aging. This uncertainty should not affect the model, which rests primarily on the content of LMS material which are detectable by RI.

VI. PERFORMANCE PREDICTION/SHADOW SPECIFICATION

If it is assumed, first, that the model described in Section II is valid for Montana roadways and, second, that the HPLC profile of a finished asphalt does not undergo major changes during aging in a pavement (Section V), then HPLC chromatograms may be used to predict the performance of pavements with respect to cracking. A logical outgrowth of this would be the construction of an asphalt specification based upon the MSD of the model asphalt. The results of a "shadow" specification study will be discussed later in this section.

All of the roadways available for the aging study (Section V) are also being used to test the ability of the HPLC method to predict the performance of recent pavements. Several of these roadways were discussed in the previous report (2). The asphalt extracted from the finished pavement and the model were analyzed and the chromatograms were compared visually. If the LMS content of the subject asphalt was the same as or less than that of the model, and if the MMS and SMS regions showed no particular anomalies, no cracking was predicted. If, on the other hand, the subject asphalt showed differences from the model, especially if it contained more LMS material than the model, the pavement was expected to crack. Some examples follow.

The Big Sky project (Figure 18) showed discrepancies with the model throughout the chromatogram. The LMS area percentage is 9.5% for Big Sky asphalt but only 7.6% for the model. This pavement would have been expected to crack. Indeed, transverse cracks ranging from 20 feet to only a few inches apart and a few longitudinal cracks appeared over the entire length of the project during the winter 1980-81. The road was newly constructed in 1977. No other cause for the cracking could be

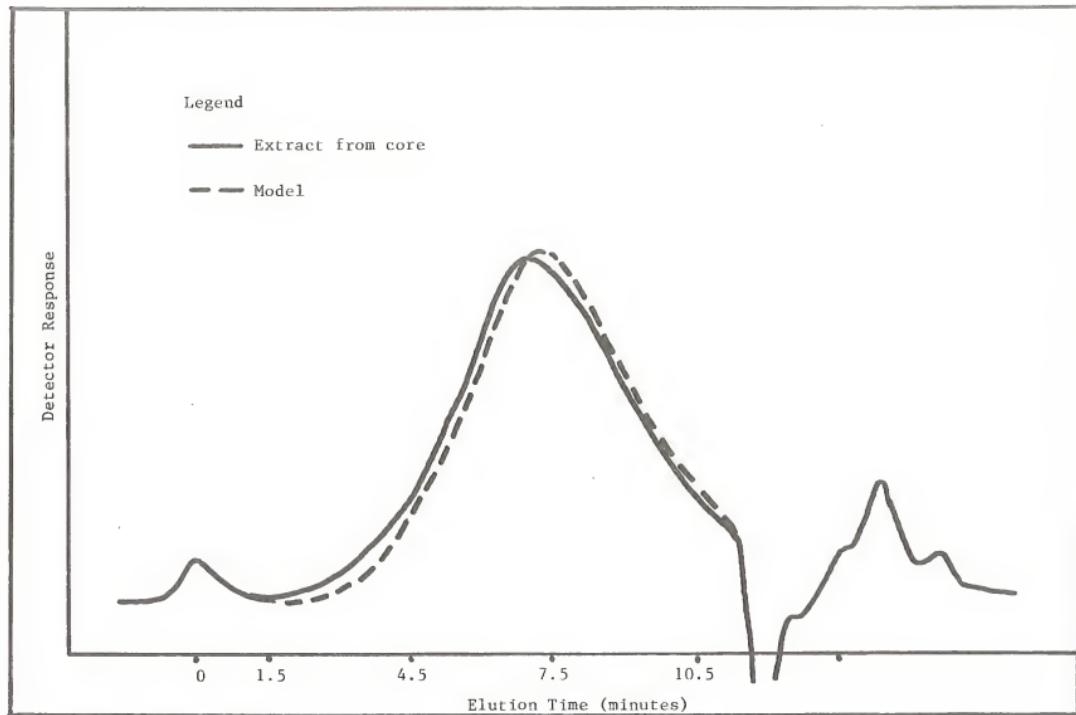


Figure 18. Comparison of Big Sky Asphalt With Model

discerned.* Asphalt from Refinery B was used and lime was added.

Similarly, US 2, Havre, Figure 19, which was constructed in 1978, was also expected to crack. A few cracks had appeared by spring of 1981. This pavement used 85-100 asphalt from refiner D.

The Two Medicine Bridge-East project, was constructed in 1978 using 120-150 asphalt from refiner D. It is also expected to crack. As of April, 1982, it was "holding up well".

The 200-300/Refiner B asphalt used in Big Sandy-Rudyard project was not expected to contribute to cracking (Figure 20). No cracking has appeared to date.

These projects and others will be monitored on a continuing basis for as long as possible.

A special group of six overlay construction projects was selected for inclusion in a shadow specification study. The samples included asphalts from all Montana refineries in 3 different penetration grades. The objective of the study was to determine the feasibility of a specification based on the HPLC profile and area percentages of the model asphalt (Section II). The results of this study are shown in Figures 21-26 and Table 13.

*Paving dates - Sept. 21 - Oct. 8, 1977
Weather - 15° - 68°, partly cloudy
Dust ratio (PMB) - <50% (66% allowable)
Voids - 0.4' PMB - 7.3%
0.2' PMS - 7.5%
Asphalt % - 5.6%
Aggregate - 1.5" PMB gr. 1
3/4" PMS gr. B
Lime - in surface, 1.5%

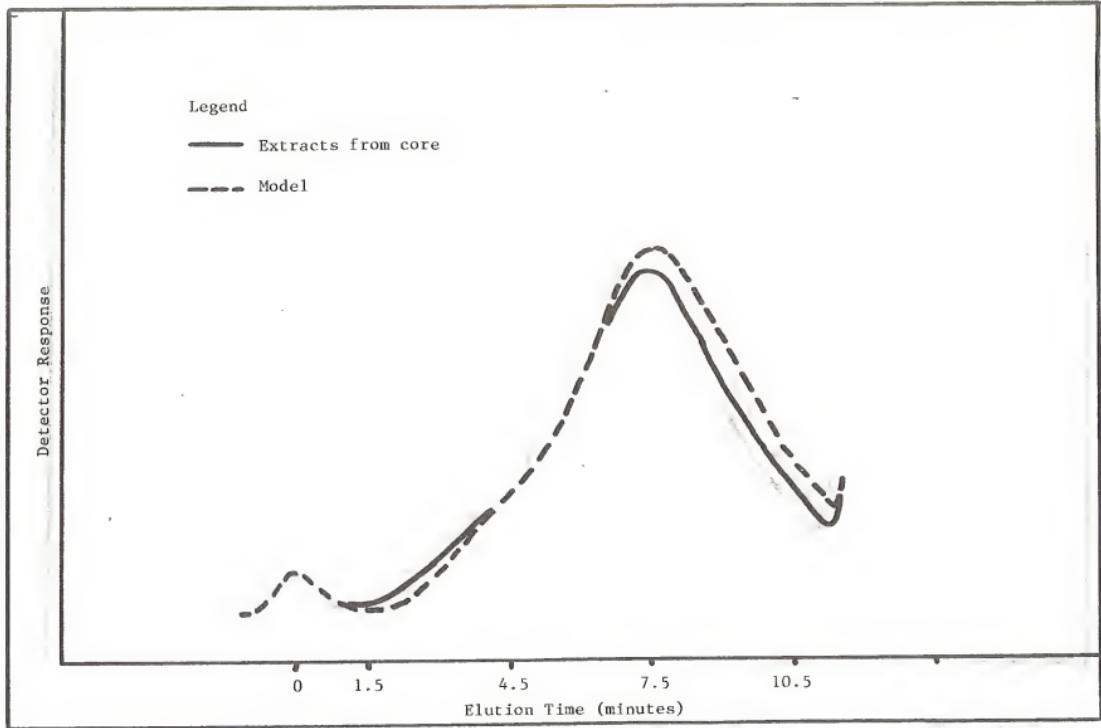


Figure 19. Comparison of US #2 - Havre Asphalt With Model

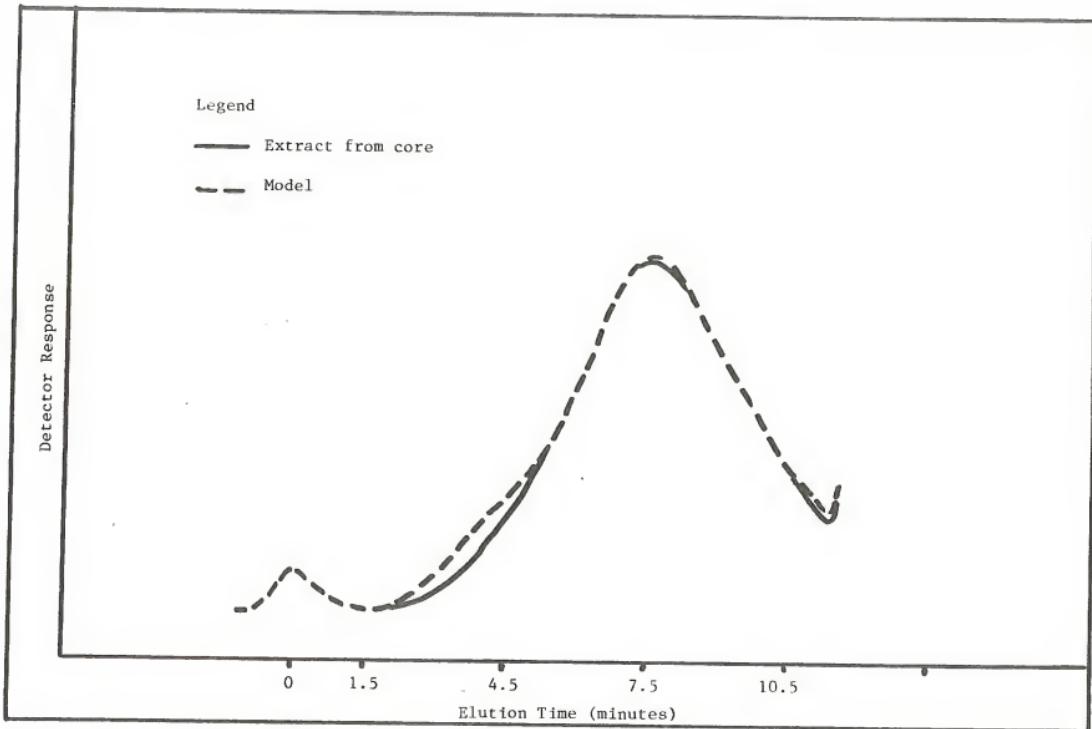


Figure 20. Comparison of Big Sandy - Rudyard With the Model

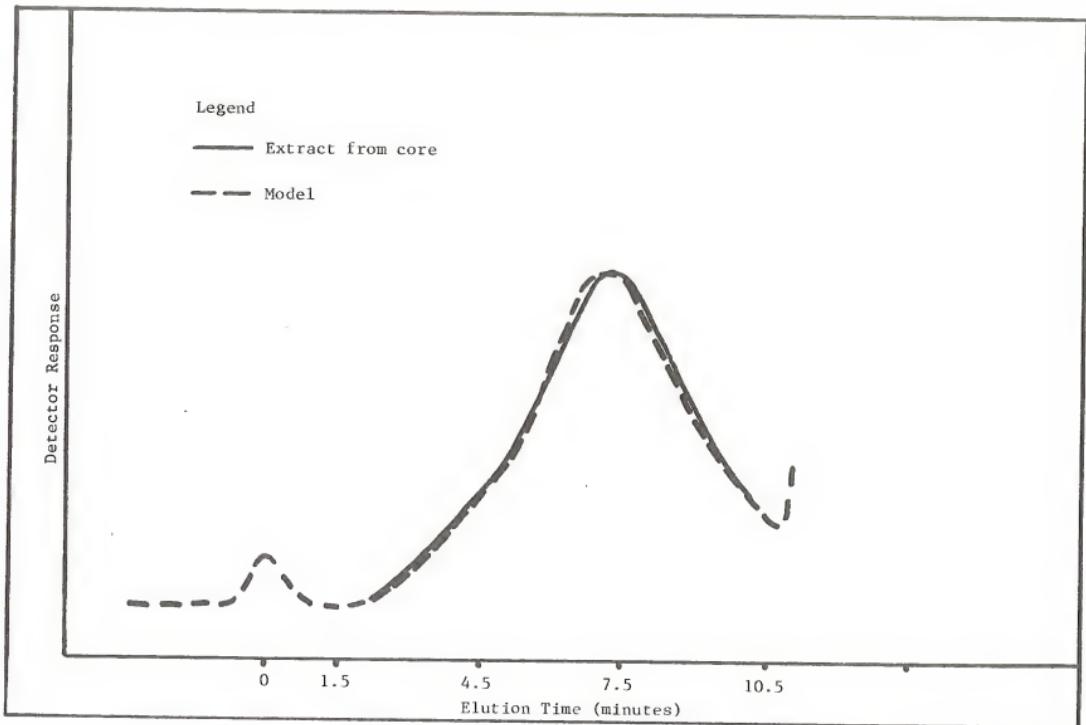


Figure 21. Shadow Specification: Comparison of Colstrip - Forsyth With the Model

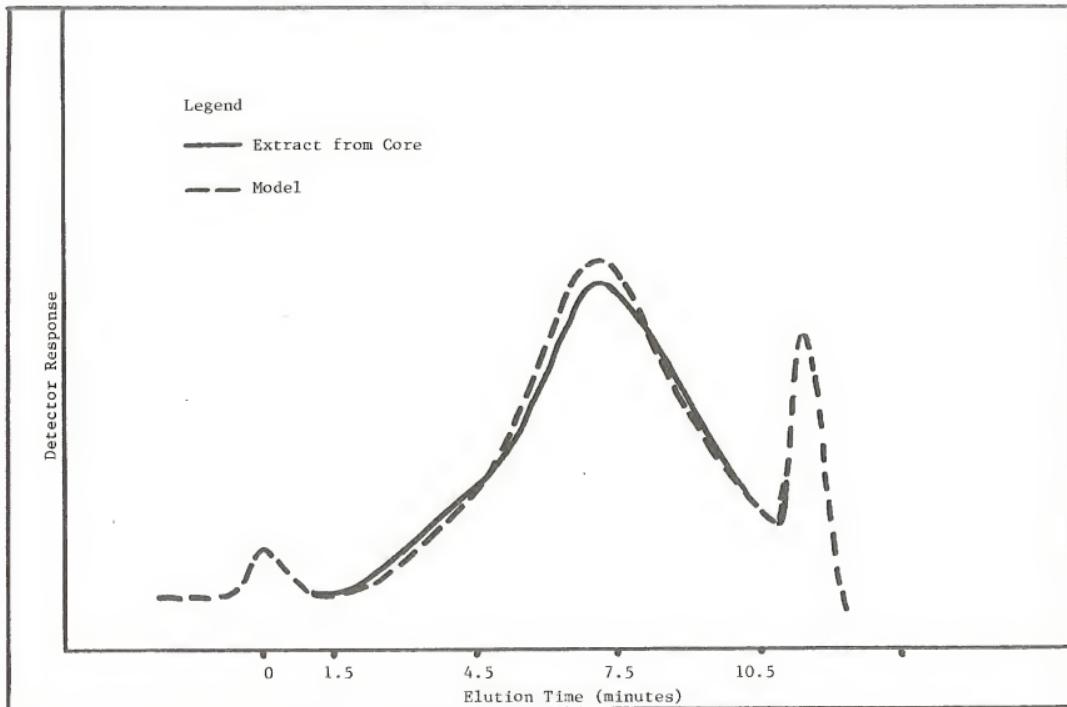


Figure 22. Shadow Specification: Glendive - Richey-2

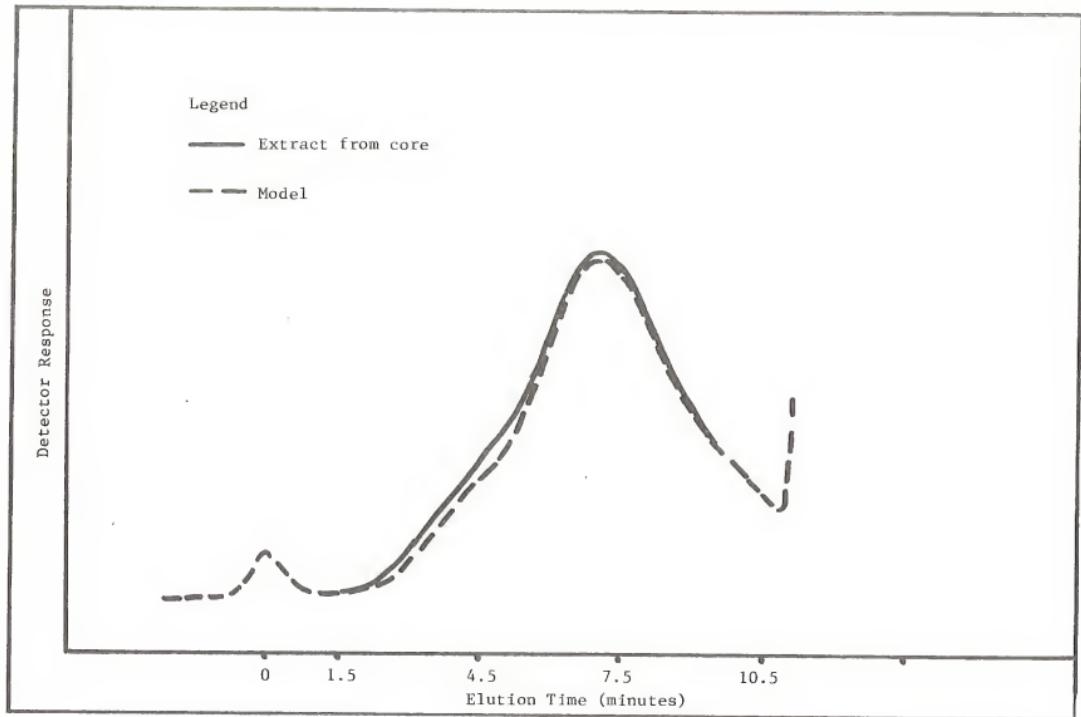


Figure 23. Shadow Specification: Comparison of Springdale - Big Timber With the Model

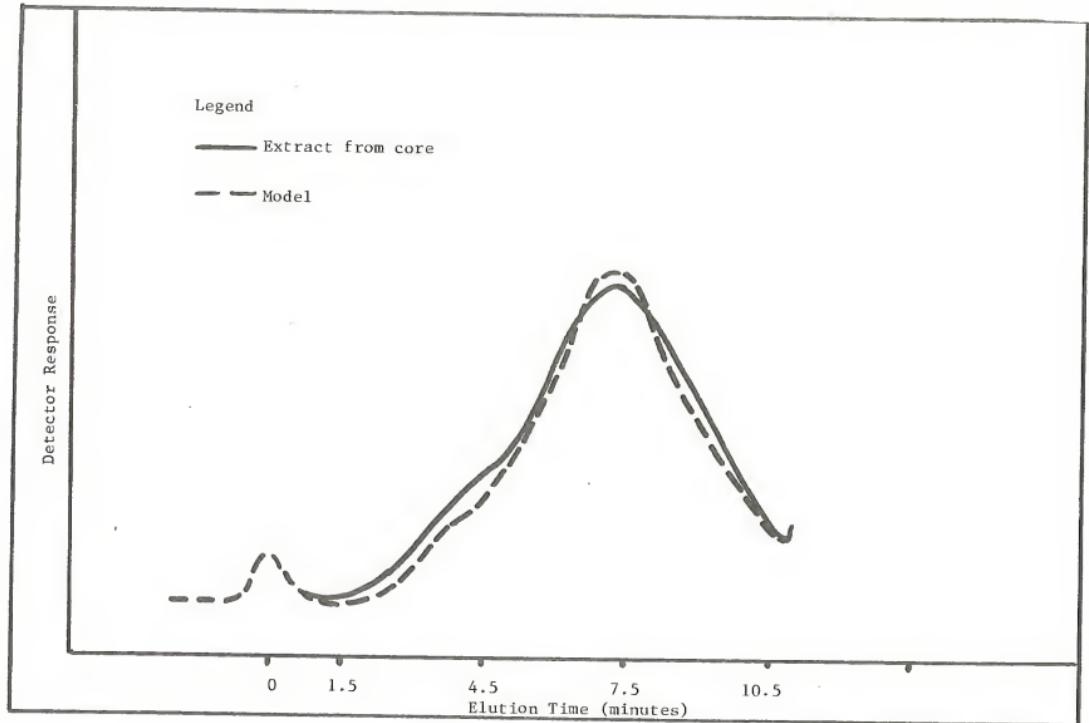


Figure 24. Shadow Specification: Comparison of 4th and 6th Avenue No. Couplet (Billings) With the Model

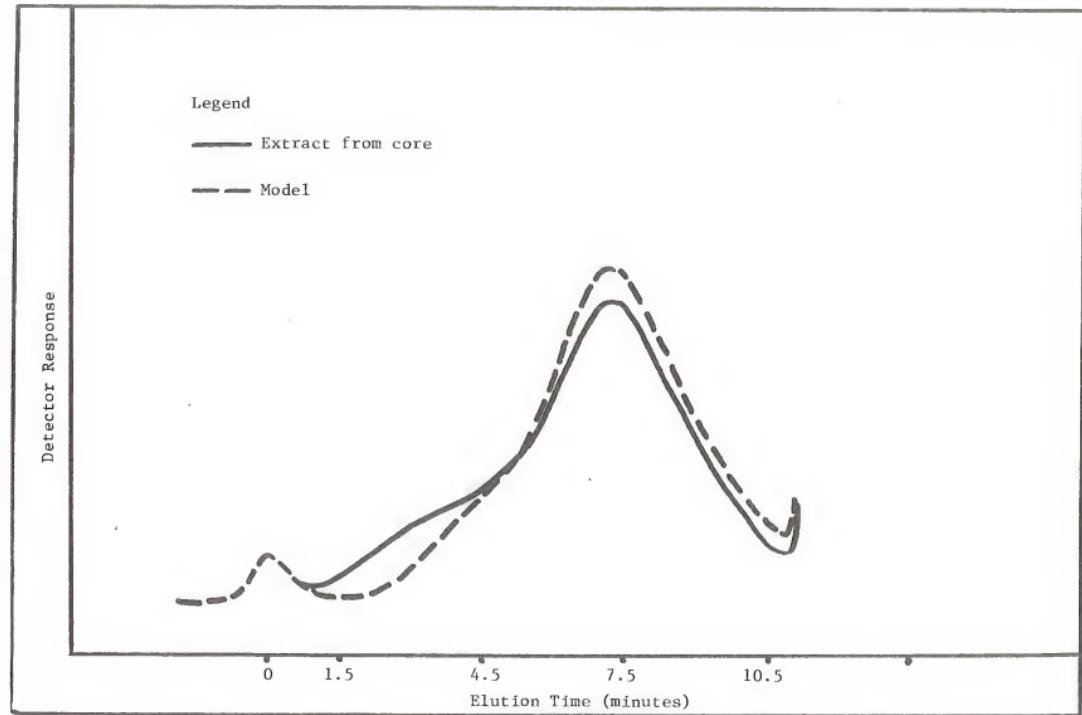


Figure 25. Shadow Specification: Comparison of Fairfield - E & W With the Model

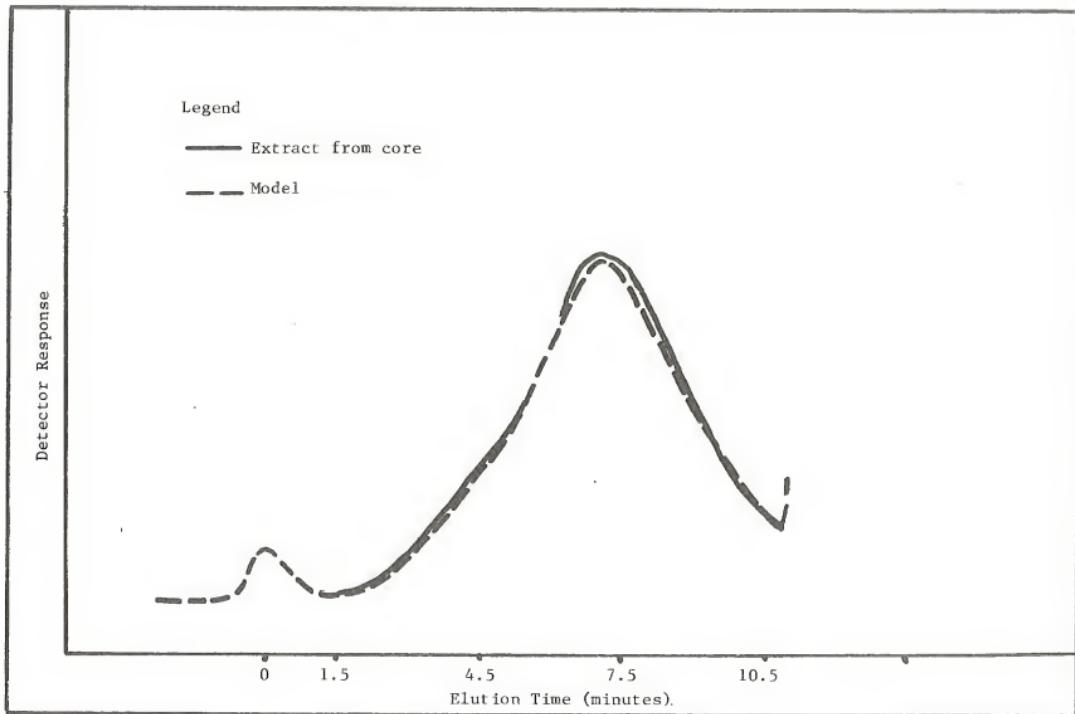


Figure 26. Shadow Specification: Comparison of Idaho Street (Kalispell) Overlay With the Model

Table 13. Shadow Specification Data

	Area %		
Sample Model Specification range	LMS 10.1 8.1-10.1	MMS 56.5 53.5-57.5	SMS 33.4 32.4-36.4
Colstrip-Forsyth (South)			
Original, Refiner B/120-150	8.2	54.4	37.4
extract from core	9.8	53.8	36.4
Idaho Street - overlay			
Original, Refiner C/85-100	9.4	54.7	35.9
extract from core	10.1	53.9	35.6
Springdale - Big Timber			
Original, Refiner A/120-150	8.5	56.4	35.1
extract from core	11.6	54.5	33.8
Glendive-Richey - 2			
Original, Refiner B/200-300	6.8	53.6	39.6
extract from core	11.5	53.1	35.4
4th and 6th Avenue No. - Couplet			
Original, Refiner B/85-100	7.7	54.2	38.1
extract from core	12.1	51.9	35.9
Fairfield - E and W			
Original, Reiner D/120-150	13.6	54.8	31.6
extract from core	16.4	52.7	30.9

Tentative limits within which the asphalt being tested should match the model were set as follows: (See page 26.)

LMS - within +0% and -2% of value for model

MMS - within +1% and -3% of value for model

SMS - within +3% and -1% of value for model

From the data in Table 13, it may be seen that the finished asphalts from Colstrip-Forsyth and Idaho Street overlay are nicely within all limits. Both would pass the specification.

Springdale-Big Timber meets the requirements for MMS and SMS ranges

but is 1.5% too high in the important LMS area. We feel this asphalt should be considered out-of-spec.

Glendive-Richey and the 4th and 6th Avenue North Couplet are both within specified limits only in the SMS region. The former exceeds the LMS limit by 1.4% and the latter by 2.0%. Both fail the specification.

The Fairfield-E and W asphalt is not within range in any of the areas and fails the specification without question.

It should be noted that these samples again show the expected increase in LMS content of from 0.7 to 4.4 on processing, thus re-emphasizing the dependence of this phenomenon on refinery source and aggregate.

VII. RECYCLING

There is a growing desire to recycle asphaltic roadways to help conserve resources, both asphalt cement and aggregate. There is a simultaneous concern that such projects be cost effective: that a reasonable service life be obtained from the recycled pavement.

During the course of studies in this laboratory, three of Montana's completed recycling projects and one scheduled for construction during the summer of 1982 have been investigated by HP-GPC. Findings concerning three of these roadways will be presented and discussed. In addition, some laboratory work based upon three of these projects will be presented.

The Idaho Street (Kalispell) project was constructed in 1980 using a hot mix method with a recycling agent designated here as "Rec. 1" (see Table 14 for mix design). The chromatograms of the components and of the recycled asphalt are shown in Figure 27. In this case, the salvaged pavement has more LMS components than does the model (>4% excess), but fewer MMS and SMS components. The recycling agent supplies mainly SMS components. These materials remain readily identifiable as SMS components in the recycled asphalt (ie., as the shoulder in the SMS region).

Table 14. Mix design for Idaho Street recycling project

Salvaged Mix	75%
Virgin aggregate	25%
Rec. 1 (by wt of salv + virgin agg)	0.46%
Virgin Asphalt (by wt of salv + virgin agg)	1.9%

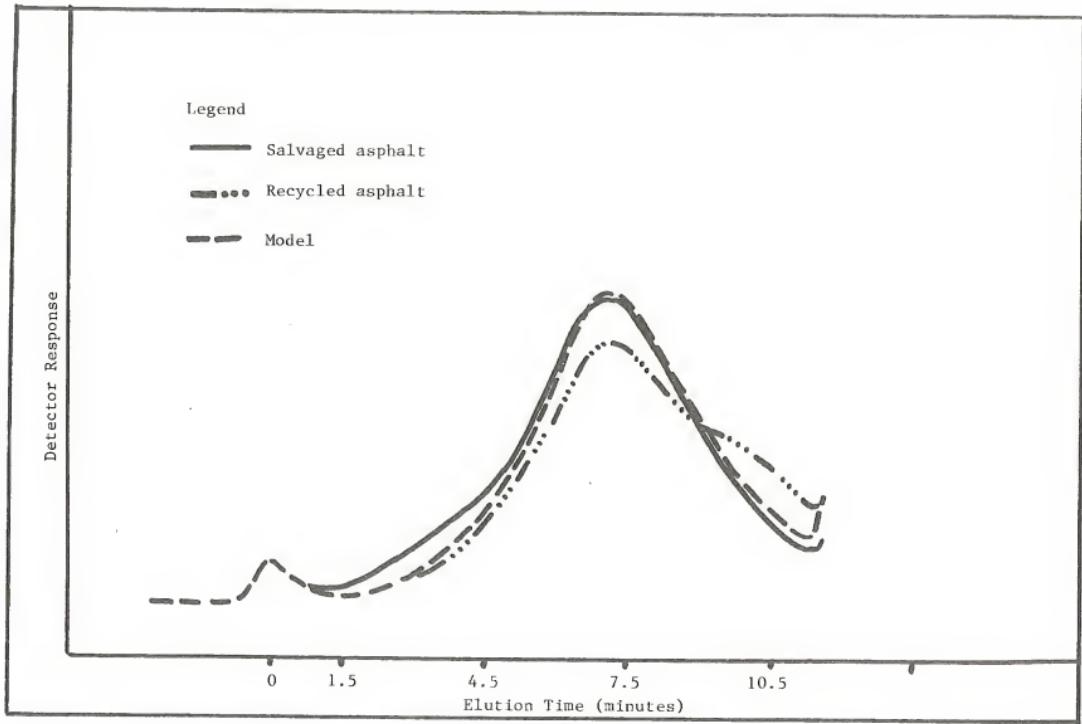


Figure 27. Montana Recycling Projects: Idaho Street (Kalispell)

Brady-North and South was constructed in 1981. Again, a hot mix method was used. Rec. 2 was selected as the recycling agent. The mix design is included in Table 15. The salvaged asphalt exceeds the

Table 15. Mix Design for Brady - N. and S. Recycling Project

Salvaged mix	70%
Virgin aggregate	30%
Rec. 2 (by wt. of salv. + virgin agg.)	0.75%
Virgin asphalt (by wt of salv. + virgin agg)	0.5%

model by 4% in the LMS region. The recycling process served to decrease the LMS in the finished core by about 2%. Nevertheless, the recycling agent remains readily identifiable in the SMS region (Figure 28).

Because the precise function of a recycling agent was unclear, a set of experiments was carried out in which the salvaged asphalt extracted from the Idaho Street project was mixed with 16% Rec. 1. Samples were heated as described in earlier sections. Some resulting chromatograms are shown in Figure 29.

Simply mixing the asphalt and recycling agent without heat ("cold" sample) does not change the size and amount of LMS components but does decrease part of the MMS while markedly increasing the amount of SMS material. After 0.5 hour at 115° both LMS and SMS appear to have decreased very slightly. After 1 hour, this process apparently has continued, but again, only very slightly. These changes are, in fact, so small as to be negligible. In other experiments in which the recycling

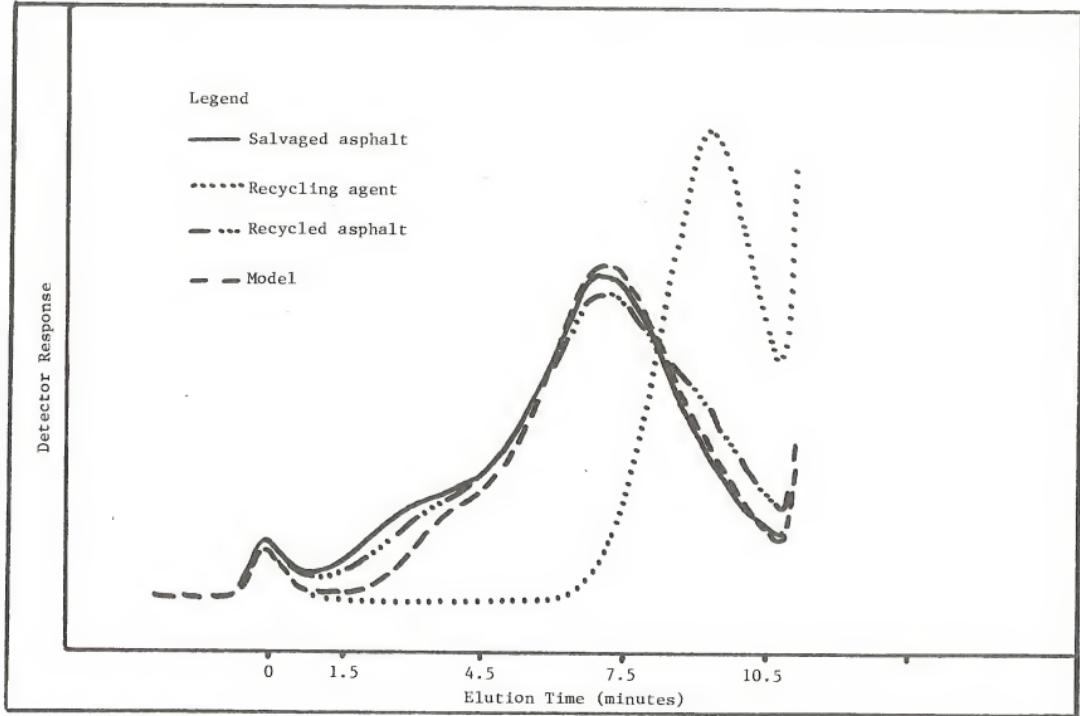


Figure 28. Montana Recycling Projects: Brady - N and S

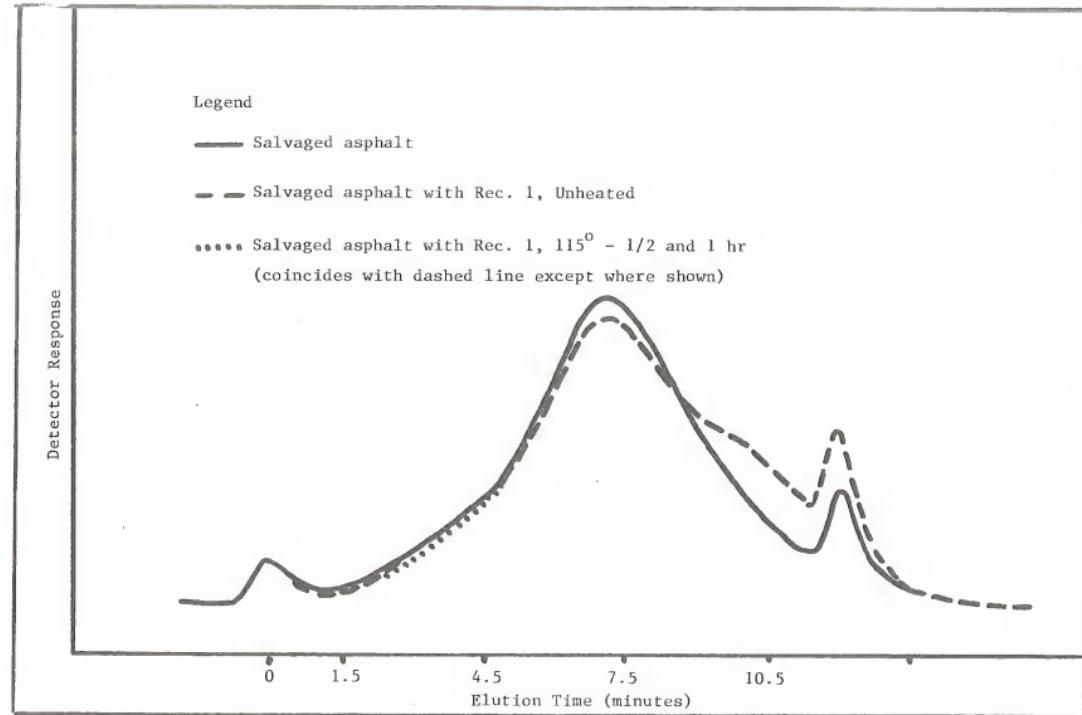


Figure 29. Effect of Recycling Agents: Rec. 1 With Idaho Street Salvaged Asphalt - No Virgin Asphalt or Aggregate Included

agent was added to crushed, salvaged pavement, then heated, similar results were noted. Therefore, it appears that this additive does not make any significant changes in the molecular size of LMS materials. The apparent changes in the overall percentage of LMS material in the recycling projects cited above are likely to be due mostly to dilution of the salvaged asphalt by the recycling agent.

Other recycling agents were tested in the laboratory. In these experiments, the Brady salvaged pavement, virgin asphalt, virgin aggregate and recycling agent were mixed in proportions given in the mix design, then were heated and sampled. A set of chromatograms for the Brady salvaged asphalt with Rec. 3 is given Figure 30. The increase in SMS components is quite striking in this case, but again, the change in LMS content is very small.

It is felt that recycling agents function primarily by increasing the penetration of the asphalt. Unfortunately, higher penetration does not necessarily coincide with a high-quality asphalt (see report, Project II). As can be seen especially in the Brady project, the LMS content of the recycled pavement still exceeds the model. The ultimate fate of the recycling agent as the pavement ages is still unknown. These projects will be monitored as part of the aging study.

The Shelby recycling project is scheduled to be completed in 1982. The chromatogram of the salvaged asphalt is compared with the model in Figure 31. The salvaged asphalt is very high in LMS and SMS but low in MMS materials. The use of a typical recycling agent is not likely to remedy the situation, if previous patterns are followed. Therefore, several laboratory experiments were undertaken to test some hypothetical solutions.

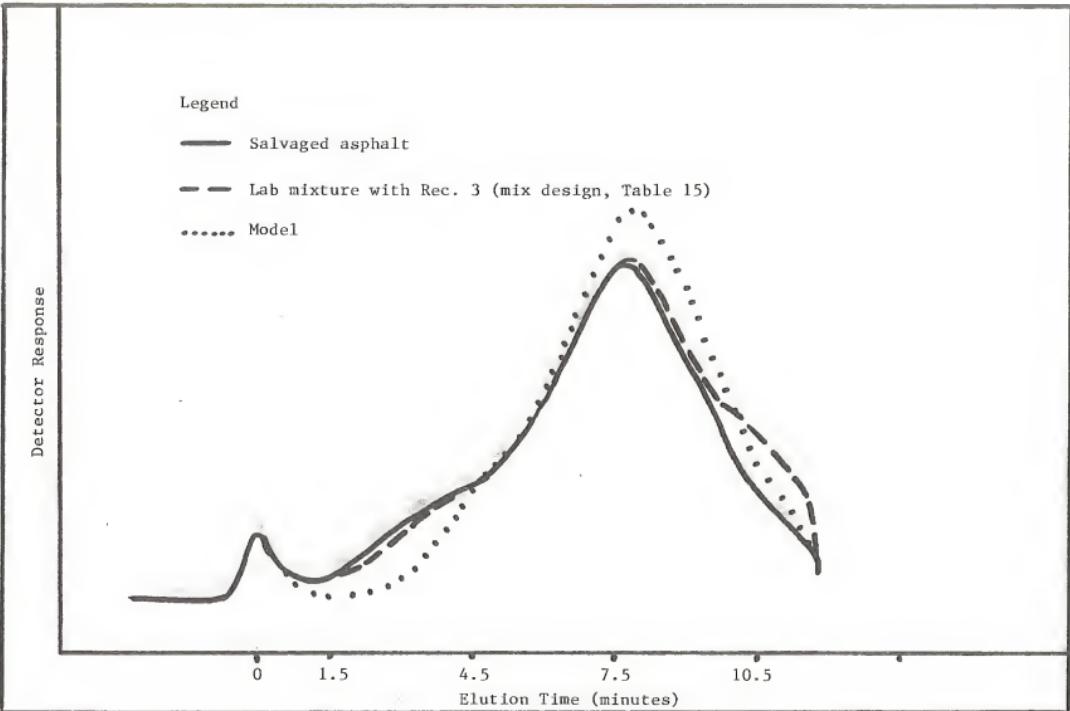


Figure 30. Laboratory Simulation of Brady Recycling Project Using Recycling Agent 3

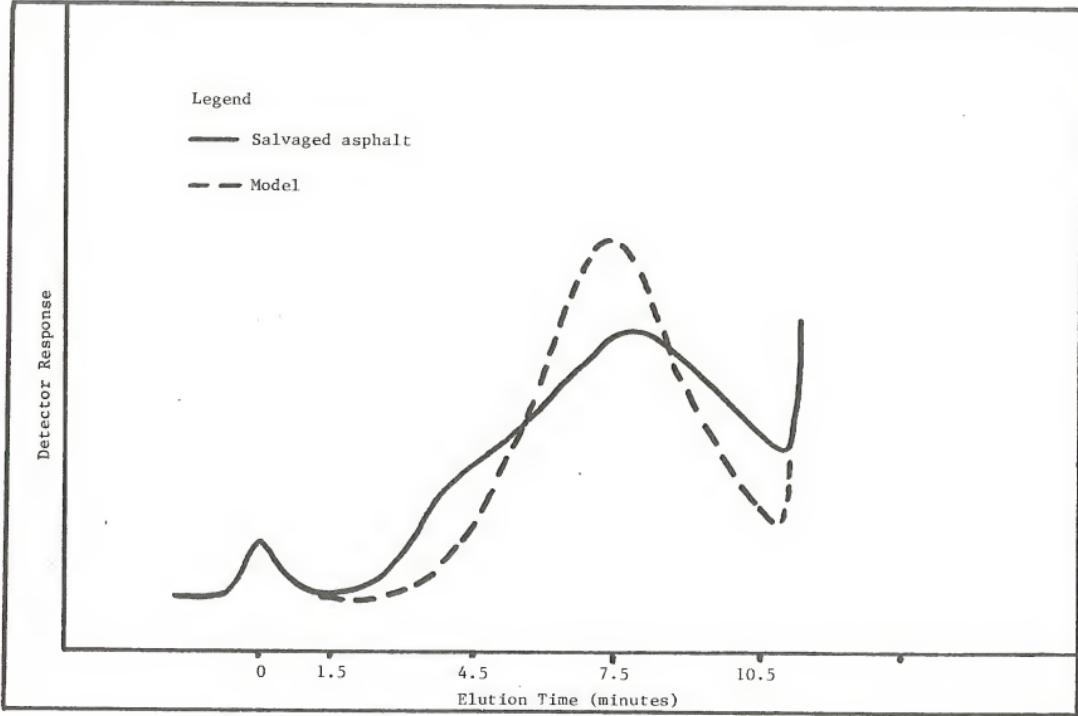


Figure 31. Shelby Recycling Project: Comparison of Salvaged Asphalt With the Model

In some areas of the country, large amounts of virgin asphalt and aggregate are mixed with the salvaged pavement in recycling projects. This approach would offer a significant advantage if, for example, an asphalt with a very low LMS content but high MMS content were mixed with the Shelby asphalt.

To test the effects of mixing different asphalts on MSD, the Shelby salvaged asphalt and a 200-300 asphalt from Refiner B were mixed in various proportions without heating. Chromatograms of these mixtures are shown in Figure 32. The smooth progression between the extremes of the pure asphalts is shown. In Table 16, the calculated LMS content of each mixture is compared with the experimental value. The error in each case

Table 16. Calculated and Experimental Percentages of LMS in
Mixtures of Salvaged Asphalt with Virgin 200-300

% in mixture Salvaged:Virgin		% LMS
	Calculated	Experimental
100:0	-	12.5
75:25	10.5	10.6
50:50	8.5	8.7
25:75	6.5	6.4
0:100	-	4.5

is less than 2%. No interaction in which molecular sizes are changed is apparent. That is, the composition of an ideal mixture of two asphalts may be calculated. This implies not only that recycled asphalts may be brought into range of the model, but also that virgin asphalts with high

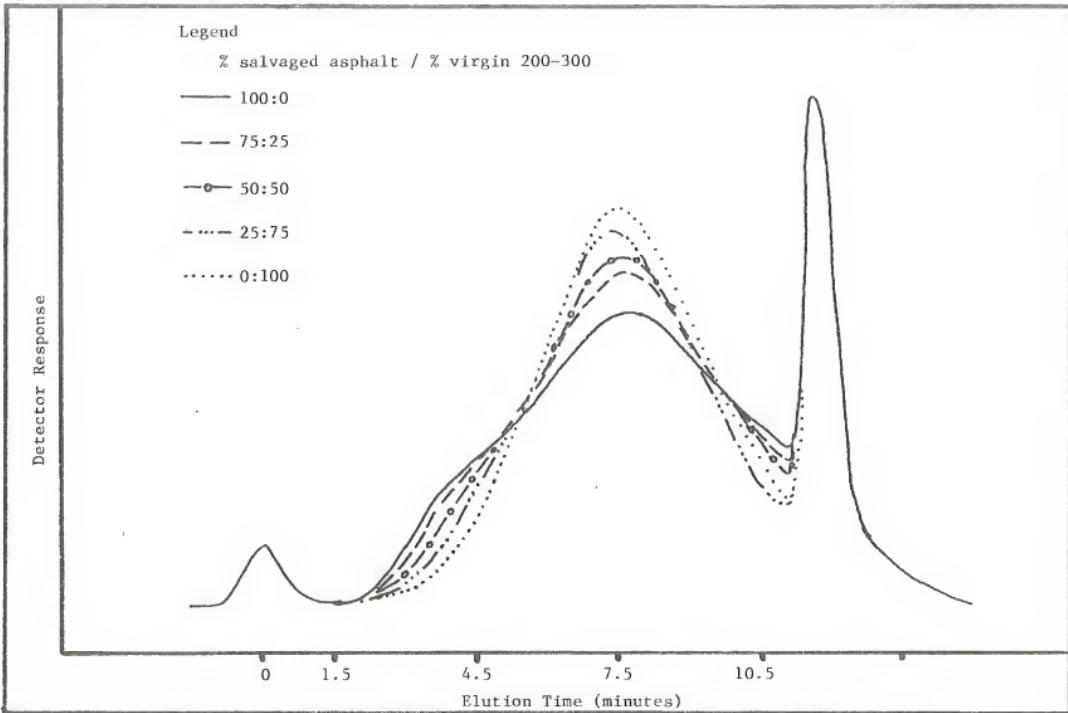


Figure 32. Effect of Combining Asphalts: Shelby Salvaged Asphalt With Virgin 200-300

LMS levels may be treated with asphalts having low LMS content to bring both closer to the model.

This idea was tested under laboratory conditions. The ideal mix was derived by calculating the ideal proportions of salvaged:virgin asphalt, then adjusting the amount of virgin aggregate required. This mixture was then prepared, heated at 115°C and sampled after 10, 15, 20 and 30 minutes.

The mixture consisted of:

<u>Mixture</u>	
crushed salvaged pavement (Shelby)	35 g
virgin aggregate - A	61.1 g
asphalt - 200-300/Refinery B	3.9 g

The chromatograms in Figure 34 shows that the laboratory mixture closely approaches the model, especially in the important LMS region. Addition of recycling agent to the mixture would be expected to further increase the amount of SMS material.

Obviously, this approach is based solely on the MSD of the asphalts involved. Other design factors must be tested. However, the most evident drawback to the use of such an approach is cost. Whether the increased cost would be offset by longer pavement life must be considered.

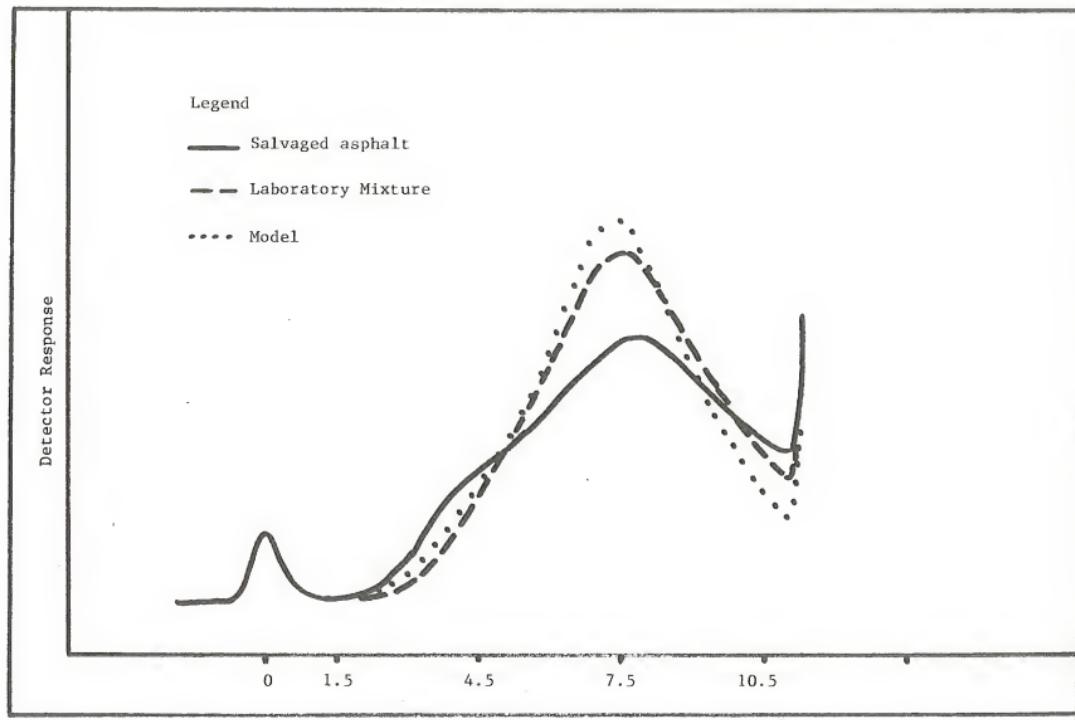


Figure 34. Comparison of Calculated Design, Prepared in Laboratory With Salvaged Asphalt and Model.
Lab Mix Design: 35% Salvaged Pavement; 61.1 % Virgin Aggregate; 3.9 % Virgin Asphalt
(200-300 Refinery B) by Total Weight of Mix

VIII. TEST SECTIONS

One of the objectives contained in the outline of this project was the construction and monitoring of a series of test sections. For a variety of reasons, this objective could not be met during the course of the project. However, 21 experimental sections are now scheduled for construction in 1983 on Interstate 90 near Big Timber, Montana. These test sections will permit comparison of the performance of four Montana-produced asphalts and mixtures of these asphalts with lime, fly ash and a recycling agent as well as carbon black and a commercial additive. Careful monitoring of these experiments will be carried out by both MDOH and this laboratory. Results will be reported elsewhere.

IX. CONCLUSIONS

During the 18-month course of this project, a great deal of experimental data has been accumulated and compiled. Much of this information serves to reinforce the notion that asphalt is a very complex mixture which is made even more complicated by its reactions with the other components of a paving mixture. Some questions have been raised which have had to remain unanswered. Nevertheless, the results demonstrate the value of the HP-GPC technique in a variety of applications to asphalt roadways. The results of the project will be summarized briefly below.

A. Adjustments and improvements have been made in methods of sample preparation and analyses. The necessity for consistency in these methods has been demonstrated. Precision of the method under the conditions used for the work in this report is within 1%.

B. The use of other solvents for the mobile phase in the HP-GPC analysis has been briefly studied. These solvents result in slightly different information than obtained with THF and some might provide valuable auxiliary data. Further study would be required.

C. Use of an ultraviolet detection system was briefly investigated. As expected, this provides different information than does the usual refractive index detector. For example, UV detects more SMS material than RI. Differences in SMS content among the four asphalts tested were shown that were not visualized by RI. After further study, UV detection might also provide valuable auxiliary information.

D. HP-GPC with RI detector was shown to detect more than 90% of actual LMS content of an asphalt.

E. Heat alone was shown to have little effect on the molecular size

distribution of asphalt. However, the addition of aggregate, lime, fly ash and antistripping agents with heat caused changes which were evidenced primarily by increases in the amount of LMS material in the asphalt, with concomitant decreases in MMS and SMS regions. No decreases in LMS content were observed. These changes were dependent on the asphalt, the aggregate and the additive. Therefore, it is not possible to predict accurately the MSD of an asphalt after processing based solely on the MSD of the untreated asphalt. However, the variety of responses shown in these experiments indicate that it is possible to engineer the asphalt to match a model by use of the proper combination of asphalt, aggregate and additive.

F. A simple method by which the effects on the MSD of asphalt of processing and lay down in the field may be duplicated in the laboratory has been developed. It requires only that the asphalt and aggregate to be used in the construction be available for testing. This may be the single most important result of this research. First, it will permit the study of a variety of parameters associated with asphalt quality. Second, it will facilitate the use of HP-GPC as a design tool because the proper combination of asphalt, aggregate and additive needed to match the model can be determined in the laboratory.

G. Early results from the aging study indicate that the MSD of an asphalt does not change a great deal during the first two years after construction. This study must be continued for 5-10 years before definitive conclusions can be reached, however.

H. The ability of the HP-GPC method and model to predict the crack-resisting performance of asphaltic pavements is also in the early stages of testing. Of the three pavements which were expected to crack, two have

done so to date. One pavement not expected to crack is performing well at this time. This phase of the study must also be continued over an extended period in order to validate the results.

I. A "shadow specification" based on the model was tested in six paving projects. Two of the asphalts met all the requirements of the model, one failed to meet only the important LMS requirement, the remainder were even more seriously out-of-specification.

J. Recycling was the subject of a number of analyses and experiments. Results from recycling projects already constructed in Montana and from laboratory simulations indicate that the usual practices cannot produce a suitable asphalt. They show that recycling agents consist primarily of SMS materials which do not interact with the salvaged asphalt to decrease the amount of LMS material but rather remain as discernable entities in the SMS region. Their chief value seems to be to increase the penetration of the asphalt, an accomplishment not guaranteed to produce a crack-resistant pavement, especially in salvaged asphalts which contain large excesses of LMS material.

Laboratory simulations show that the MSD of a mixture of asphalts can be calculated from the area percentages of the individual asphalts and their proportions in the mixture. Furthermore, the proportions of an ideal mixture of salvaged asphalt and virgin asphalt can be calculated so that the model may be closely approached.

K. HP-GPC in the present configuration does not appear to be suitable for analysis of asphalt mixtures containing sulfur, rubber and carbon black.

APPENDIX A. Extraction Method

Ultrasonification was used to extract asphalt from cores and other asphalt-aggregate mixtures. The upper 1/2 inch of the core was removed to avoid interference from roadway contaminants. Each lift (pavement layer) was sampled separately and material from the interfaces between lifts was avoided. The sample was crushed, 200-300 grams were placed in a large (1000 ml) beaker. Tetrahydrofuran (THF) (300-500 ml) was added to the sample. The mixture was sonicated for about 40 minutes using Bronwill "Biosonik" ultrasonification apparatus. The mixture was filtered through a glass fibre filter (Whatman GF1A) and the aggregate was washed with additional THF. This process was repeated if asphalt remained on the aggregate. The bulk of THF was removed from the solution using a rotary evaporator (Buchi) at 40°C for about 10 minutes. Remaining solvent was removed by continued rotovapping at 90°-100°C for about 40 minutes. The recovered asphalt was stored in tins or tightly capped glass vials.

APPENDIX B. Methods for Laboratory Simulation of Field Effects

To simulate in the laboratory the effects of processing and lay-down in the field on the molecular size profile of asphalt, samples of the asphalt, aggregate and any other additive actually used in the field are required.

Two hundred grams of aggregate were heated to temperature (115°C or 163°C) in an oven under ambient atmosphere (the oven of a gas chromatograph was used). Twelve grams of asphalt (6% by wt of aggregate) were warmed to 90°C in a 500 ml Teflon beaker, the heated aggregate was added and the mixture stirred with a stainless steel spatula to coat the aggregate. (1.5% lime by weight of aggregate was added with the aggregate when required. Fly ash would be added to the aggregate, whereas antistripping agents would be added to the asphalt.) A small sample was removed immediately ("0 hour") and the mixture was returned to the oven. Subsequent samples were collected every 5 minutes for 60 minutes at 115°C and for 30 minutes at 163°C. The samples were stirred occasionally during the heating period.

After cooling the samples, about 100 ml THF were added to each. The mixtures were allowed to stand about 30 minutes before filtering through glass fibre filters (Whatman GF1A). The aggregate was thoroughly washed with additional THF. Solvent was removed as described in Appendix A. Recovered asphalt samples were stored in tightly capped glass vials.

APPENDIX C. Methods for Determination of the Effects of
Heating and Additives

In these experiments, the following combinations were tested:

- 1) Each of 4 asphalts - ambient atmosphere
 - nitrogen atmosphere
 - additional air
- 2) Each of 4 asphalts with each of 5 aggregates, ambient atmosphere
(6% asphalt by weight of aggregate)
- 3) Each of 4 asphalts with lime (25% lime by weight of asphalt)
ambient atmosphere
- 4) Each of 4 asphalts with each of 5 aggregates and lime, ambient
atmosphere (6% asphalt and 1.5% lime by weight of aggregate)
- 5) Each of 4 asphalts with fly ash, ambient atmosphere (25% fly ash
by weight of asphalt)
- 6) Each of 4 asphalts with each of 5 aggregates and fly ash,
ambient atmosphere (6% asphalt and 1.5% fly ash by weight of
aggregate)
- 7) Each of 4 asphalts with antistripping agent 1, ambient
atmosphere (1.5% Asa by weight of asphalt)
- 8) Each of 4 asphalts with each of 5 aggregates and Asa 1, ambient
atmosphere, (1.5% by Asa by weight of asphalt)

For each of these combinations, the following samples were
collected for HP-GPC analysis:

- 1) Untreated asphalt
- 2) Unheated mixture
- 3) Heated mixture (115°C or 163°C) immediately after mixing

4) Heated mixture (115°C or 163°C) after 0.5 hour of continued heating

5) Heated mixture (115°C or 163°C) after 1 hour of continued heating

Samples without aggregate were prepared by heating asphalt in an oven to temperature. Additives were stirred in at that point and sampling was begun. Samples were stirred occasionally during the heating period.

For mixtures requiring aggregate, the asphalt and aggregate were heated separately in an oven. Lime and fly ash, when required, were mixed with the aggregate before heating. Antistripping agent was added to the heated asphalt just before mixing with aggregate. When asphalt and aggregate had reached 115°C (or 163°C), the aggregate was added to the asphalt (in a Teflon beaker) and stirred to coat the aggregate. A sample was taken immediately and the mixture was returned to the oven for continued heating.

Asphalt was extracted and prepared as described in Appendix B.

APPENDIX D. Methods of Analyses by HP-GPC

The high performance (or pressure) gel permeation chromatography instrument (Waters Associates) consisted of high pressure pump (M 6000 A), an injector (Model U6K), a detector (Model R 401 differential refractometer), a microprocessor (Data Module) and 6 μ -Styragel columns arranged in the order: one 10^3 Å, four 500 Å, one 10^5 Å. UV-grade THF was used as mobile phase.

A solution of 1% polystyrene (MW = 35,000) and 0.06% toluene in THF was prepared. This solution was used in the preparation of 0.2% solutions of asphalt. To prepare a 0.2% solution of asphalt for analysis, a small amount (0.02 - 0.025 gm) of asphalt, prepared according to the procedure in Appendix A, was accurately weighed into a small vial. A volume of the polystyrene-toluene/THF solution determined by ml solvent = $\frac{\text{grams of asphalt}}{.002}$ was accurately added by means of a buret.

The instrument was operated in accordance with manufacturer's instructions. One ml of sample was injected into the system. Pumping rate was 2 ml/min, chart speed was 1 cm/min. Refractive index detector attenuation was 8X.

The temperature of columns, detector and mobile phase was controlled at 26°C by means of a system of tubing and a constant temperature bath.

The microprocessor was programmed to find the area of successive slices of the asphalt chromatogram 0.3 minutes wide. The percentage of the total asphalt area contained in each of three 3-minute segments of the curve was calculated separately.

Precision in consecutive analyses of a sample asphalt should be within 1%.

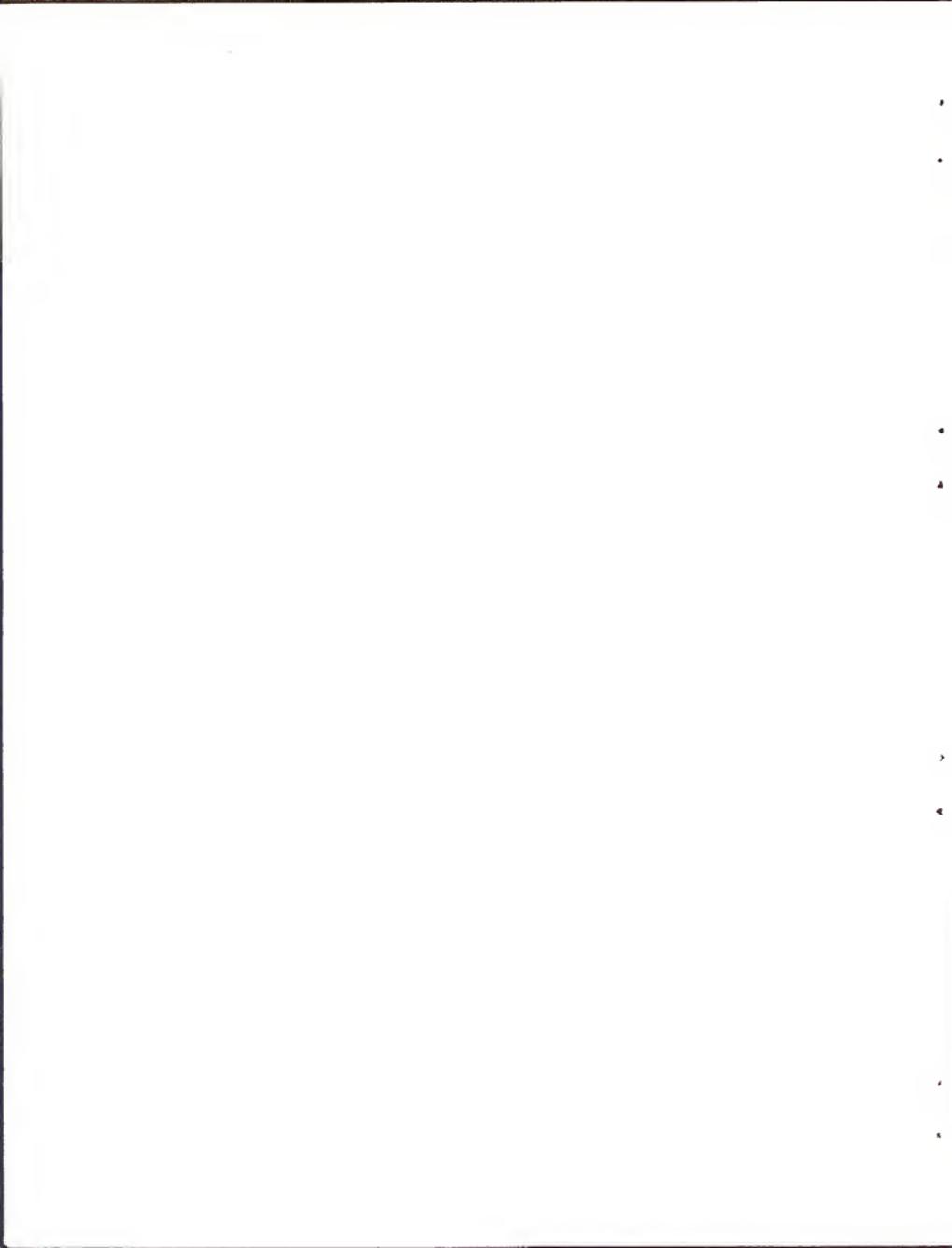
APPENDIX E. Petrographic Analyses of Sample Aggregates

% Components

Sample	Grade	igneous	sandstone	quartzite	misc	Rating
A	3/4" PMS, Gr C	0	53.8	46.2	0	good
B	3/4" PMS, Gr B	24.1	55.0	17.8	3.1\$ (chert)	good
C	1 1/2" PMB	9.8	30.3	59.4	trace (chert)	fair-poor
D	3/4" PMS, Gr C	25.8	17.7	46.6	9.9 (chert)	poor
E	1 1/2" PMB	27.9	4.6	67.5	0	fair

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